# THE LAWS GOVERNING THE RATE AT WHICH METALS DISSOLVE IN CONCENTRATED ACIDS

## II.   THE SOLUTION RATES AND DISSOLUTION POTENTIALS OF CHROMIUM AND IRON.

### Ya. V. Durdin

As we have stated in our previous report [1], two types of curves $\underline{v}(\underline{c})$ are found when metals are dissolved in concentrated acids, representing the rate of dissolution of the metal as a function of the acid concentration: $\underline{v}(\underline{c})$ curves exhibiting a maximum and those without one.

It has been shown in our previous report [1] that curves possessing a maximum reflect the superposition of a secondary phenomenon - the precipitation of a deposit of a salt of the metal upon the latter's surface. The fundamental behavior patterns involved in the rates at which metals dissolve as a function of the acid concentration are therefore reflected by the curves having no maximum.

An essential factor is the fact that (as has been noted in the same report) the general shape of these curves is the same for various metals: Cd, Al, Fe, and Cr, the appearance of the $\underline{v}(\underline{c})$ curves reflecting the step-by-step variation of the dissolution rate with the acid concentration, while the curves approach a straight line in sulfuric acid.

Tsentnershver thought that the functions of $\underline{v}(\underline{c})$ obtained by him for the dissolution of cadmium [2], aluminum [3], and tin [4] could be represented by the equation:

$$\underline{v} = kc^{n}, \tag{1}$$

where $\underline{n}$ = 4 for Cd and 3 for Al. Since a function of this sort was wholly out of line with the variation of the specific conductance of hydrochloric acid with its concentration, Tsentnershver concluded that only alloys dissolved in accordance with an electrochemical mechanism, while the pure metals (which he assumed the Kahlbaum Cd and Al he had tested were) dissolve via a peculiar mechanism, which he called 'chemical', in which the metal is dissolved as a result of its interaction with the acid anion [5]. This led to a sharp duality in dealing with the rates of dissolution of metals, not only in concentrated acids, but in the general case as well, since it did not follow from Tsentnershver's hypothesis that his chemical mechanism could change to an electrochemical one in dilute acids or salt solutions.

These difficulties were aggravated by the lack of a definition of the line of demarcation between a pure metal and an alloy, inasmuch as Tsentnershver used the term 'pure metal' for the metals supplied by the Kahlbaum firm that he employed in his tests, though their purity is highly relative. It may be added that if we use the Tsentnershver mechanism, we have to assume that the dissolution of cadmium or tin in hydrochloric acid entails the simultaneous collision of four chlorine atoms with an atom of the metal in the space lattice, which is highly improbable. Moreover, Tsentnershver based his mechanism upon the fact

that the dissolution rates of the metals he investigated obeyed Equation [1].
According to that equation, log $\underline{v}$ must be a linear function of log $\underline{c}$. But actually
if we use Tsentnershver's own data on the dissolution rates of cadmium [2]
and aluminum [3,6] in plotting a lg $\underline{v}$ - lg $\underline{c}$ curve, we get broken lines, the
slopes of the various sections of these lines ranging from $\underline{n}$ = 5.8 to $\underline{n}$ = 2.7
in the interval from 6N to 12N HCl. The value of $\underline{n}$ =4 used by Tsentnershver thus
is some sort of mean of these values, possessing no definite physical significance.
The same sort of picture is found in the case of aluminum.

In the present pape we endeavor to show that the patterns of behavior
observed when chromium and iron are dissolved in hydrochloric and sulfuric
acids conform to generalized electrochemical theory.

## The Treatment of the Laws Governing the Dissolution Rates of Chromium and Iron in Hydrochloric and Sulfuric Acids as Based Upon Generalized Electrochemical Theory.

According to the data on the rates of dissolution of chromium and iron
obtained in our laboratory [7,8], the rates at which these metals dissolve
in hydrochloric and sulfuric acids may be regarded as unaffected by the
diffusion process, provided the solution is stirred intensively enough.
If we assume that the kinetic energy of the process of ion transfer between
the cathodic and anodic areas via conductance is practically equal to zero,
then the generalized electrochemical theory asserts that the dissolution
rates of chromium and iron must be governed by the rates at which the electrode
processes - the cathodic process in which hydrogen is evolved and the anodic
process in which the metal ions leave the solution - take place.

The feasibility of explaining the behavior patterns governing the rates
at which metals are dissolved in concentrated acids on this basis was first
demonstrated in the author's paper 'The electrochemical mechanism of the
dissolution of metals in acids' [9]. This paper, which dealt in general with
the feasibility of handling the laws governing the dissolution rates of metals
by means of the laws governing the rate at which electrode processes take place,
quoted excerpts from the above-mentioned paper by A. Markiyevich and the
present author on the rates at which chromium and iron dissolve in hydrochloric
and sulfuric acids by way of illustrating this possibility, it being shown
that the behavior patterns observed in the dissolution of chromium can be
treated like the laws governing the rate at which the cathodic process of
hydrogen evolution takes place. It was shown, in particular, that the
exponential shape of the $\underline{v}(\underline{c})$ curve for the dissolution of chromium in
hydrochloric acid may be explained as a result of the decrease in the energy
of hydration of the hydrogen ions in concentrated solutions of hydrochloric
acid and a corresponding decrease in the energy of activation of their dis-
charge.

In that same paper an experimental method of comparing the $\underline{v}(c)$ curves
for the rates of metal dissolution and the rates of the cathodic process of
hydrogen evolution was employed to substantiate these assumptions. In this
instance we made use of the circumstance that, according to our results [7],
the dissolution potential of chromium referred to a saturated calomel electrode
was practically constant throughout the range of 1N to 10N acid, this held
for both the hydrochloric and the sulfuric acids. With this as a basis we
ran tests in which we measured the rate of the cathodic evolution of hydrogen
as a function of the concentration of the hydrochloric and sulfuric acids,
the potential of the cathode referred to the saturated calomel electrode
being kept constant. A comparison of the resultant $\underline{v}(\underline{c})$ curves for the

for rate of dissolution of chromium indicated that the shapes of the two curves were fully alike qualitatively. These experiments, made to plot the $\underline{v}(\underline{c})$ curves for the cathodic evolution of hydrogen, were preliminary tests. To corroborate our findings we made more precise determinations of the same function with a dropping mercury electrode; the qualitative nature of these curves was found to be the same as in the preliminary tests. The $\underline{v}(\underline{c})$ curves secured in these tests are plotted in Fig. 1. For convenience in comparison, the $\underline{v}(\underline{c})$ curves for the dissolution of chromium and iron taken from our papers written in collaboration with A. Markieyvich [7] and M. Oranskaya [8] are reproduced in Fig. 2 (the experimental points being omitted for the sake of simplicity ). Comparison of these graphs clearly indicates the complete qualitative similarity between the shape of the $\underline{v}(\underline{c})$ curves for the dissolution of the metals and that of the corresponding curves for the velocity of the cathodic evolution of hydrogen.



Fig. 1

We thus could regard it as an established fact that the qualitative nature of the $\underline{v}(\underline{c})$ curves, without any maximum, plotted for the dissolution of metals in hydrochloric and sulfuric acids, not only does not contradict the generalized electro-chemical theory, but, on the contrary, is in full accordance with it.

For further study of this problem it was desirable to shift from a qualitative to a quantitative comparison of these same behavior patterns. With this as our objective, we began to make preparations for further, more precise experiments to determine the variation of the velocity of the cathodic evolution of hydrogen with the concentration of hydrochloric and sulfuric acids; this project was interrupted by the war, however.



Fig. 2

At the present time we are making use of the data on hydrogen over-voltage provided in the papers by Z. Iofa and A.N. Frumkin [10, 11, 12] for this purpose.

### Attempted Quantitative Comparison of the Rate of Dissolution of Chromium and Iron as a Function of the Acid Concentration with the Corresponding Cathodic Process Rates

The cited papers by Z. Iofa and A. Frumkin give figures for the hydrogen overvoltage at mercury and lead cathodes in hydrochloric, sulfuric, hydrobromic, and perchloric acids of various concentrations. In order to derive the velocity
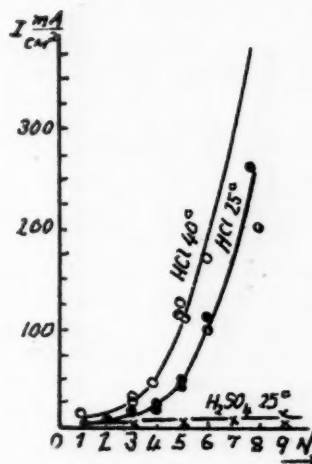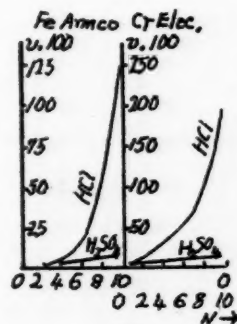
of the cathodic evolution of hydrogen as a function of the concentration of the respective acid for a fixed cathode potential referred to the saturated calomel electrode, which we were interested in, we had to have the equilibrium potentials of a hydrogen electrode referred to a saturated calomel electrode in these same solutions.

The determinations of these potentials for solutions of hydrochloric and  sulfuric acids at concentrations ranging from 1N to 0.1N and at temperatures of 20, 40, and 60°C  were made by V.G. Levina under the supervision of the author.

These measurements were made in parallel tests run with systematically platinized and checked platinum electrodes. As in our metal dissolution experiments, the other electrode was a saturated calomel electrode. The tests were run in a water thermostat, the temperature of which was kept constant within ±0.1°C.  To prevent the hydrogen chloride that collected under the dome of the hydrogen electrode from being blown out of the concentrated solutions of hydrochloric acid, the hydrogen was first passed through a vessel containing the same solution of hydrochloric acid and immersed in the same thermostat. The acid concentrations were determined before and after each run. The potentials were measured by the usual compensation method with an accuracy of 1 mv, inasmuch as high precision was unnecessary for our purposes and, besides, the experimental margin of error proved to be greater than that figure. As a rule, the discrepancy between the potentials as measured in two parallel tests did not exceed 1-3 mv, though discrepancies of as much as 10 mv were observed in some tests in which concentrated solutions were employed. Neither damage to nor poisoning of the hydrogen electrode can have been responsible for these discrepancies, inasmuch as identical results were always secured when the hydrogen electrode was replaced by another. We suppose the reason behind these potential fluctuations is fluctuation in the value of the diffusion potential within the electrolytic switch. The electrolytic switch used was a $\pi$-shaped glass tube, sectioned off at its midpoint by a three-way glass stopcock. Before a run was started, the acid solution to be used in the test was pumped into one of the tubes connected to this stopcock, while a saturated solution of potassium chloride was pumped into the other. The stopcock itself was always moistened with the saturated solution of potassium chloride. The stopcock was kept closed during the measurement. We found that if the electrolytic switch was withdrawn, emptied, and then refilled (or simply replaced by a similar switch) after the potential of the hydrogen electrode had been measured, the potential of the hydrogen electrode would hardly vary at all, 1-3 mv at most, though greater fluctuations, as high as the indicated 10 mv, were found in some instances. The potentials measured at 20°C  in these tests are listed in Table 1.

Using the figures in Table 1 for the equilibrium potential of the hydrogen electrode and the figures for the hydrogen overvoltage given in Z.A. Iofa's paper for various concentrations of hydrochloric and sulfuric acids, we can readily calculate the variation of the velocity of the cathodic evolution of hydrogen with the concentrations of these acids, provided the cathode potential referred to the saturated calomel electrode is kept constant. We shall begin by considering the case of hydrochloric acid. The figures covering the evolution of hydrogen at a lead cathode are given in Table 2, and at a mercury cathode in Table 3.

In these tables:

1) $N$ = normality of the acid.

2) $\underline{E}^O$ = equilibrium potential of the hydrogen electrode (referred to a saturated calomel electrode) in the acid of given concentration at 20° . The values of $\underline{E}^O$ are taken from Table 1. We stipulate that in the present paper it will be more convenient for us to introduce different notation for potentials referred to the calomel electrode, which we shall denote by $\underline{E}$, and for the potential jump at the metal-solution boundary, for which we retain the notation $\varphi$.

Table 1.

Equilibrium Potentials of a Hydrogen Electrode (Referred to a Saturated Calomel Electrode) in Hydrochloric and Sulfuric Acids at 20 °C    (With Reversed + Sign)

| | $\underline{N}$ | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $E^O$ Volts | HCl | 0.249 | 0.231 | 0.217 | 0.204 | 0.194 | 0.184 | 0.175 | 0.166 | 0.158 | 0.149 |
| | $H_2SO_4$ | 0.263 | 0.249 | 0.236 | 0.228 | 0.222 | 0.215 | 0.208 | 0.202 | 0.197 | 0.192 |

Table 2

| 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|---|---|---|---|---|---|---|
| N HCl | $E^O$ | $\Delta\varphi'$ | b | E | $\Delta\varphi''$ | W |
| 1 | 0.249 | 1.055 | 0.119 | 1.304 | 1.055 | 1 |
| 3 | 0.217 | 1.005 | 0.142 | 1.304 | 1.087 | 3.8 |
| 5 | 0.194 | 0.935 | 0.140 | 1.304 | 1.110 | 18 |
| 7 | 0.175 | 0.865 | 0.138 | 1.304 | 1.129 | 82 |
| 10 | 0.149 | 0.755 | 0.135 | 1.304 | 1.156 | 930 |

Table 3

| 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|---|---|---|---|---|---|---|
| N HCl | $E^O$ | $\Delta\varphi'$ | b | E | $\Delta\varphi''$ | W |
| 1 | 0.249 | 0.940 | 0.119 | 1.189 | 0.940 | 1 |
| 3 | 0.217 | 0.863 | 0.140 | 1.189 | 0.972 | 6 |
| 5 | 0.194 | 0.770 | 0.124 | 1.189 | 0.995 | 65 |
| 7 | 0.175 | 0.714 | 0.114 | 1.189 | 1.014 | 430 |
| 10 | 0.149 | 0.660 | 0.106 | 1.189 | 1.041 | 4000 |

3) $\Delta\varphi'$ = hydrogen overvoltage at the mercury or lead cathode in hydrochloric acid at the stated concentration, the current density being $I$ = $10^{-4}$ amp/sq cm. We have taken the values of $\Delta\varphi'$ from papers by Z. Iofa [12], Z. Iofa [10], and Z. Iofa and A. Frumkin [11].

5

4) $\underline{b}$ = a constant from Tafel's equation. The values of $\underline{b}$ were taken from the same papers by Z. Iofa.

5) $\underline{E}$ = the constant cathode potential for which the C.D. is computed for various concentrations of hydrochloric acid. The value of $\underline{E}$ was taken as the cathode potential in 1N hydrochloric acid at a C.D. of $\underline{I} = 10^{-4}$ A/cm$^2$. For the lead electrode, we see from Table 2 that $\underline{E}$ is 0.249 + 1.055 = 1.304 V, while Table 3 shows that for the mercury electrode E = 0.249 + 0.940 = 1.189 V.

6) $\Delta\varphi''$ = the hydrogen overvoltage in hydrochloric acid of various concentrations for the potential $\underline{E}$.

7) $\underline{W}$ = the comparative increase in the rate of the cathodic process in shifting from 1N hydrochloric acid to hydrochloric acid of the stated concentration. The values of $\underline{W}$ can be readily found from the values of $\Delta\varphi'$ and $\Delta\varphi''$ in the table columns and from Tafel's equation:

$$\Delta\varphi = a + b \log \underline{I},$$

whence

$$\frac{\Delta\varphi'' - \Delta\varphi'}{b} = \log \frac{I''}{I'} = \log W,$$

where $\underline{I}'$ is the C.D. corresponding to a constant value of the cathode potential $\underline{E}$ in hydrochloric acid, and $\underline{I}''$ is the C.D. for the same value of $\underline{E}$ in hydrochloric acid of the stated concentration. The analogous figures for the cathodic evolution of hydrogen at a lead electrode in sulfuric acid are given in Table 4.

Table 4

| 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|---|---|---|---|---|---|---|
| N H$_2$SO$_4$ | E$^O$ | $\Delta\varphi'$ | b | E | $\Delta\varphi''$ | W |
| 1 | 0.263 | 1.060 | 0.119 | 1.325 | 1.061 | 1 |
| 3 | 0.236 | 1.056 | 0.119 | 1.325 | 1.089 | 1.9 |
| 5 | 0.222 | 1.054 | 0.120 | 1.325 | 1.103 | 2.6 |
| 8 | 0.202 | 1.050 | 0.120 | 1.325 | 1.123 | 4.0 |

The values of $\underline{E}^O$ in this value are taken from Table 1. The values of $\Delta\varphi$ and $\underline{b}$ are taken from the paper by Z. Iofa [12], p.120, Table 4.*

Figure 3 reproduces the curves that express the variation of $\underline{W}$ with the concentration of hydrochloric and sulfuric acids for a lead cathode. These curves have been plotted from the figures in Tables 2 and 4. At first sight these curves are quite similar to those reproduced in Fig. 2, though it is not hard to see that this is not quite the case quantitatively speaking. This is strikingly illustrated by the figures in Table 6. This table has been compiled from the data in Tables 2,3, and 5. Table 5 gives the figures for the rates of dissolution of chromium and iron (Armco and light sheet) in hydrochloric and sulfuric acids of various concentrations, according to the findings reported in our papers with A. Markiyevich [7] and M. Oranskaya [8]. As always, the velocity $\underline{v}$ in this

---

*It should be stated that in Iofa's paper the hydrogen overvoltages at a lead electrode in H$_2$SO$_4$ are given only for 0.1N, 1N, 8N, 15N, and 20N H$_2$SO$_4$. We see from Table 5 that the total change in overvoltage is 0.01 volt from 1N to 8N sulfuric acid. Using this figure, we calculated $\Delta\varphi$ for 3N and 5N H$_2$SO$_4$, setting $\Delta\varphi/\Delta$ = const = 0.0012 though we could have set $\Delta\varphi'$ = const for this case without any special loss in our calculations. In the range from 8N to 15N H$_2$SO$_4$, the change in the hydrogen overvoltage is somewhat higher, totaling 0.055 volt, according to the data in the above paper, the proportion of the change in overvoltage attributable to the 8-10N H$_2$SO$_4$ range being unknown, so that in our calculations we confined ourselves to the 1N - 8N sulfuric acid range.

table is expressed as cubic centimeters of hydrogen evolved per minute per sq cm of metal surface. Table 6 gives the relative rates $\underline{W}$ for these metals and for the cathodic processes, the values of $\underline{W}$ in Section I of this table representing the ratio of the rate of dissolution of the given metal or the rate of the cathodic process in hydrochloric acid of the stated concentration to the rate in 1N acid, while in Section II $\underline{W}$ represents the ratio of the rate in acid of the stated concentration to 5N acid. The figures in Table 6 show that, notwithstanding the outward similarity of the $v(\underline{c})$ curves, the extent of the change in velocity with $\overline{ac}id$ concentration is different in every case, the rate of metal dissolution rising much more slowly than the rates of the cathodic processes. This difference is diminished at high concentrations of hydrochloric acid, as we see in Section II of the table, the discrepancy being least for the Armco iron.* An altogether differ-ent state of affairs prevails in the sulfuric acid, as we see from Table 7, which lists the values of $\underline{W}$, representing the ratio of the velocity of the cathodic process or the metal dissolution rate in sulfuric acid of the stated concentration to the corresponding rates in 2N sulfuric acid (the rate at which iron dissolves in 1N sulfuric acid was not measured).
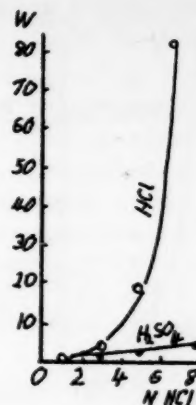
Fig. 3

## Table 5

### Dissolution Rate of Chromium and Iron in Hydrochloric and Sulfuric Acids

(Chromium at $40°$, iron at $60°$**)

Hydrochloric Acid

| Acid normality | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 N |
|---|---|---|---|---|---|---|---|---|---|---|
| Chromium | 7.3 | 11(5) | 17 | 24 | 33 | 45 | 66 | 95 | 125 | 190 |
| Armco Iron | - | - | - | 2.3 | 5.5 | 15 | 30 | 50 | 77 | 126 |
| Light sheet iron | 8.0 | 13(5) | 17 | 24 | 36 | 56 | 85 | 130 | 230 | 430 |

Sulfuric Acid

| Acid normality | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 N |
|---|---|---|---|---|---|---|---|---|---|---|
| Chromium | 4.3 | 5.7 | 6.6 | 7.5 | 8.4 | 9.4 | 11.0 | 12.5 | 14.5 | 16.5 |
| Armco Iron | - | (1.8) | (2.5) | (3.0) | (4.0) | (4.5) | (5.5) | (6.4) | (7.0) | (8.0)* |
| Light sheet iron | - | 12.5 | 16.0 | 20 | 25 | 30 | 35 | 40 | 46 | 52 |

We see in Table 7 that in sulfuric acid the velocities of all the processes we have been considering change comparatively slowly with acid concentration,

---

*As will be shown in a forthcoming paper, this fact may be due to a drop in the rate at which Armco iron dissolves at comparatively low acid concen-trations, due to secondary phenomena.

**The figures for Armco iron in sulfuric acid are preliminary, as was stipulated in the paper in question [8].

7

the changes being approximately identical[*], which is of especial interest to us.

Table 6

### Comparative Rates of Dissolution of Metals and of Cathodic Evolution of Hydrogen in Hydrochloric Acid

| | Acid normality | 1 | 3 | 5 | 7 | 10N |
|---|---|---|---|---|---|---|
| I | $\overline{W}$, Hg cathodic process | 1 | 6.1 | 65 | 480 | 4000 |
| | $\overline{W}$, Pb cathodic process | 1 | 3.8 | 18 | 82 | 930 |
| | $\overline{W}$, light sheet Fe | 1 | 2.1 | 4.5 | 10.6 | 54 |
| | $\overline{W}$, Cr | 1 | 2.3 | 4.5 | 9.0 | 26 |
| II | $\overline{W}$, Hg cathodic process | - | - | 1 | 7.4 | 62 |
| | $\overline{W}$, Pb cathodic process | - | - | 1 | 4.5 | 52 |
| | $\overline{W}$, light sheet Fe | - | - | 1 | 2.4 | 12 |
| | $\overline{W}$, Armco Fe | - | - | 1 | 5.5 | 23 |
| | $\overline{W}$, Cr | - | - | 1 | 2.0 | 5.8 |

### Table 7

| Acid normality | 2 | 3 | 5 | 8 |
|---|---|---|---|---|
| $\overline{W}$, Pb cathodic process | 1 | 1.3 | 1.8 | 2.8 |
| $\overline{W}$, light sheet Fe | 1 | 1.3 | 2.0 | 3.2 |
| $\overline{W}$, Armco Fe | 1 | (1.3) | (2.1) | (3.5) |
| $\overline{W}$, Cr | 1 | 1.2 | 1.5 | 2.2 |

Summing up, we may say that although there is a marked qualitative analogy between the $v\,(\underline{c})$ curves for metal dissolution and those for the cathodic evolution of hydrogen, there is a considerable quantitative difference between the rates at which these process rates change with the concentration of hydrochloric acid, the cathodic process rates rising with the acid concentration more rapidly than do the metal dissolution rates in the instances we have investigated. In sulfuric acid, on the other hand, we have a fairly satisfactory quantitative, as well as qualitative correspondence between the $v(\underline{c})$ functions for the dissolution of the various metals and those for the cathodic evolution of hydrogen.

### The Causes Governing the Variation of the Rates at Which Chromium and Iron Dissolve With the Concentration of Hydrochloric and Sulfuric Acids

The foregoing makes it evident that the explanation of these causes must be based upon the laws governing the velocity of the cathodic evolution of hydrogen in concentrated solutions of hydrochloric and sulfuric acids.

We can use the experimental findings and the theory of hydrogen overvoltage in concentrated acids set forth in the cited papers by Z. Iofa and A. Frumkin.

---

[*]It should be stated that the potential of chromium was practically identical in both hydrochloric and sulfuric acids, as has been demonstrated in our researches on chromium and iron [7,8]; the same holds true of the potential of Armco iron in hydrochloric acid. In sulfuric acid, the potential of Armco iron dropped slightly, by some 20 mv, in the transition from 2N to 10N sulfuric acid; the potential of light sheet iron, measured at the start of the test, changed by the same amount. The feasibility of ignoring this slight change in potential is dealt with in our forthcoming papers.

In these papers [10,11] an equation is derived for the velocity of the cathodic evolution of hydrogen in concentrated acids:

$$\underline{v} = \text{const } [H^\cdot] \underline{f}\, \frac{\alpha'}{H'}\, e^{\frac{[\alpha\varphi + \psi_1(1-\alpha)]F}{RT}} \tag{2}*$$

In Equation (2) $[H^\cdot]$ is the hydrogen-ion concentration in the solution: $\underline{f}$ is the activity coefficient of these ions; $\varphi$ is the 'metal-solution' potential; $\psi_1$ is the sharp potential gradient between the layer at a distance of one ionic radius from the metal's surface and the solution; if $\psi'$ is the sharp potential gradient in the Helmholtz double layer, then $\varphi = \psi' + \psi_1$ ; $\alpha$ is a constant, usually assumed to equal 0.5; $\alpha'$ is also a constant, whose value is likewise close to 0.5, according to the experiments made by Iofa and Frumkin [11], p. 281.

According to Equation (2), in concentrated solutions a change in the hydration energy of the hydrogen ions and an adsorption of the ions in the boundary layer** may affect the kinetics of discharging these ions, as well as a change in cathode potential $\varphi$ and in the hydrogen-ion concentration $[H^\cdot]$. The factor $\underline{f}\alpha'$ in Equation (2) makes allowance for the effect of a change in the hydration energy of the hydrogen ions upon the velocity of the cathode process. In this light, the value of $\alpha' = 0.5$ signifies that a change in the hydration energy of a hydrogen ion has the same effect upon the energy level of the transitional discharge state of the hydrogen ion as does a change in the energy level of the hydrogen ion due to a change in the cathode potential ($\alpha = 0.5$).

The effect of adsorption of the anions is represented by the potential $\psi_1$.. As shown in the researches of Z. Iofa and A. Frumkin, the expression they secured for the hydrogen overvoltage by a suitable transposition of Equation (2) makes it very easy to describe and explain the qualitative picture existing in the complicated system of behavior patterns manifested by hydrogen overvoltage in concentrated acids. This equation cannot, however, be regarded as quite accurate, quantitatively speaking. It may be that this inaccuracy is due in part, as has been indicated in that same paper [11], to the fact that the adopted representation of the double layer is still too crude, but, in addition, the use of this equation for precise quantitative computations is also complicated by the fact that the activity of the individual ion (hydrogen), an unknown factor, enters into the equation.

In their papers, Z. Iofa and A. Frumkin have on occasion made an attempt to escape this difficulty by using the mean activity of hydrochloric acid instead of the activity of the hydrogen ion. It is admitted that from the quantitative standpoint such a substitution is likewise insufficiently rigorous. Lastly, this equation cannot be used for quantitative calculations in most cases when nonmercury cathodes are employed, owing to our ignorance of the value of $\psi_1$. At first glance, the use of Equation (2) in dealing with the laws governing the rates at which metals dissolve involves even greater difficulties, since, in addition to what has been outlined above, any change in the acid concentration will affect the diffusion potential at the boundary between the acid and the potassium chloride solution (in the calomel electrode circuit). As a result, the changes in the cathode potential, measured with reference to the calomel electrode, may differ by an appreciable and unknown amount from the changes of the potential $\varphi$ entering into Equation (2). It might well be thought that the sum total of all

---

*In the cited papers by Z. Iofa and A. Frumkin, $\varphi$ and $\psi_1$ have the opposite sign in this equation.

**More precisely, the anion concentration in the adsorption layer.

these difficulties would not merely make it wholly impossible to use Equation (2) for the qualitative treatment of the laws governing the rate at which a metal dissolves, but might even interpose considerable uncertainty in their qualitative elucidation.

Upon closer examination of the problem, however, we find that Equation (2) may be so transformed for dealing with the problems with which we are concerned as to eliminate the difficulties arising from the unknown activity of the hydrogen ions and the diffusion potential, thus making use of this equation considerably easier.

In this transformation, we set $\alpha = \alpha' = 1/2$ in Equation (2) and assume that $[H^\cdot]\, \underline{f}^{1/2} = [H^\cdot]^{1/2}\cdot a^{1/2}$, where $\underline{a}$ is the activity of the hydrogen ion. We can then rewrite Equation (2) as follows:

$$v = \text{const } [H^\cdot]^{1/2}\cdot a^{1/2}\cdot e^{\frac{F\varphi}{2RT}}\cdot e^{\frac{F\psi_1}{2RT}} \tag{3}$$

We then agree to consider the relative velocity $\underline{W}$, discussed above, rather than the absolute velocity. From Equation (3), we get the logarithm of $\underline{W}$ as:

$$\ln W = \frac{1}{2}\ln \frac{[H^\cdot]'}{[H^\cdot]} + \frac{1}{2}\ln \frac{a'}{a} + \frac{F\Delta\varphi}{2RT} + \frac{F\Delta\psi_1}{2RT} \tag{4}$$

where

$$W = \frac{v'}{v}\; ; \; \Delta\varphi = \varphi' - \varphi; \; \Delta\psi_1 = \psi_1' - \psi_1.$$

In these equations the variables bearing a prime refer to the acid of stated concentration, those without a prime mark referring to the acid of standard concentration, for which we assume that $\underline{W}$ equals unity. We denote the diffusion potential at the boundary between the acid and the saturated solution of potassium chloride by $\varphi_D$, so that:

$$E' - E = \Delta E = \Delta\varphi + \Delta\varphi_D. \tag{5}$$

where $\underline{E}' - \underline{E}$ is the difference between the cathode potential (referred to the saturated calomel electrode) in the acid solution of given concentration ($\underline{E}'$) and that in the standard solution ($\underline{E}$); $\Delta\varphi$ is the corresponding difference in the sharp potential gradient at the metal-solution boundary; and $\Delta\varphi_D$ is the corresponding difference at the liquid-liquid boundary. Provided the cathode potential is constant, referred to the calomel electrode, i.e., provided $\Delta\underline{E} = 0$, we get:

$$\Delta\varphi = -\Delta\varphi_D.$$

Inserting this value of $\Delta\varphi$ in Equation (4), we get an expression for $\ln \underline{W}$ when the cathode potential referred to the saturated calomel electrode is constant:

$$\ln W = \frac{1}{2}\ln \frac{a'}{a} + \frac{\Delta\psi_1 F}{2RT} + \frac{1}{2}\ln \frac{[H^\cdot]'}{[H^\cdot]} - \frac{F\Delta\varphi_D}{2RT} \tag{6a}$$

or when $\Delta\psi_1 = 0$

$$\ln W = \frac{1}{2}\ln \frac{a'}{a} + \frac{1}{2}\ln \frac{[H^\cdot]'}{[H^\cdot]} - \frac{F\Delta\varphi_D}{2RT} \tag{6b}$$

We do not know the change in the diffusion potential, which is a factor in this equation. Ignorance of this variable makes it impossible to determine the value of $\ln a'/a$ from the data for the equilibrium potential of the hydrogen electrode in the corresponding acid solutions. But in this case these two difficulties cancel each other out. In fact, the difference between the two equilibrium hydrogen-electrode potentials, referred to the saturated calomel electrode, in these two acid solutions is:

$$\Delta E^\circ = \Delta \varphi^\circ + \Delta \varphi_D,$$

while

$$\Delta \varphi^\circ = - \frac{RT}{F} \ln \frac{a'}{a},$$

so that

$$\ln \frac{a'}{a} = - \frac{F}{RT} \Delta E^\circ + \frac{F}{RT} \Delta \varphi_D.$$

Substituting this expression for $\ln \frac{a'}{a}$ in Equation (6a) and combining the $\frac{F}{RT} \Delta \varphi_D$ terms, we get:

$$\ln W = \frac{F}{2RT} \Delta E^\bullet + \frac{F}{2RT} \Delta \psi_1 + \frac{1}{2} \ln \frac{[H^\circ]'}{[H^\circ]} \tag{7}$$

or

$$\log W = \frac{1}{2} \left( \log \frac{[H^\circ]'}{[H^\circ]} - \frac{\Delta E^\circ F'}{RT} + \frac{\Delta \psi_1 F'}{RT} \right) \tag{8a}$$

At $\Delta \psi_1 = 0$,

$$\log W = \frac{1}{2} \left( \log \frac{[H^\circ]'}{[H^\circ]} - \frac{\Delta E^\circ F'}{RT} \right), \tag{8b}$$

where $\underline{F}' = F \cdot 0.434$.

Equation (8) is therefore largely free of the uncertainties involved in the use of Equation (2).

The paper by Z. Iofa and A. Frumkin [11] gives values of $\psi_1$ for a mercury electrode. Using these values, we can make a sample calculation of $W_{Hg}$. This calculation has no special significance for us. We could have confined ourselves to Equation (8) for the qualitative inferences with which we are concerned. We perform this calculation largely to obtain a clearer idea of the problem*.

The values needed for this calculation are listed in Table 8. The values of $\psi_1$ have been taken from the paper by Z. Iofa and A. Frumkin [11], though with a plus sign, as we have stipulated, rather than with a minus sign as given in that paper. The values of $\Delta E^\bullet$ have been calculated from the data in Table 1, while the values of $\underline{W}$exper. have been taken from Table 3. We obtained the values of $\underline{W}_{calc.}$ from Equation (8).

## Table 8

|  | 1 | 3 | 5 | 7 | 10 |
|---|---|---|---|---|---|
| $\psi'$ | 0.078 | 0.149 | 0.206 | 0.277 | 0.348 |
| $\Delta \psi_1 / 0.058$ | 0 | 1.22 | 2.21 | 3.44 | 4.66 |
| $\Delta E^\circ / 0.058$ | 0 | 0.552 | 0.948 | 1.28 | 1.72 |
| $\lg \frac{H^\circ}{H}$ | 0 | 0.484 | 0.703 | 0.848 | 1.00 |
| W calc. | 1 | 13 | 85 | 600 | 5000 |
| W exper. | 1 | 6 | 65 | 430 | 4000 |

The figures in Table 8 indicate that the values of $\underline{W}_{calc.}$ are in good agreement with those of $\underline{W}_{exper.}$ We see from this table that the rapid rise in the velocity of the cathodic evolution of hydrogen at a mercury cathode with increasing concentration of sulfuric acid, represented by an exponential curve, is governed chiefly by a rise in the value of $\psi_1$, representing the effect of anion adsorption. The potential change $\Delta E^\bullet$ $\}^{**}$ which is probably governed by an increase in the activity of the

*It should be noted that the values of $\psi_1$ cited in the paper by Z. Iofa and Frumkin are for potentials at the maximum on the electrocapillary curve, rather than a constant potential referred to the calomel electrode. Not too much importance need be attributed to this fact in the present case, inasmuch as the very same paper states that the decrease of the hydrogen overvoltage in concentrated acid solutions is only slightly affected by the potential of the cathode.

**The foregoing indicates that the variable $\Delta E^\circ$ likewise covers the change in the diffusion potential at the liquid-liquid boundary.

hydrogen ions, likewise exerts an appreciable effect. The least effect is
produced by an increase in the concentration of these ions* . These con-
clusions are in general agreement, of course, with those inferred in the
cited papers by Z. Iofa and A. Frumkin from these authors' findings on the
hydrogen overvoltage at a mercury cathode in hydrochloric acid.

As we see in Table 2, the velocity rises somewhat less with a lead cathode
than with a mercury one as we pass from 1N to 10N hydrochloric acid. Equa-
tion (8a) indicates that the reason for this must be a smaller change in the
value of $\psi_1$ when a lead electrode is used. When sulfuric acid is used,
the anion adsorption in the acid concentration range up to 8N apparently has
no effect upon the hydrogen overvoltage at a lead cathode, according to the
findings reported in the same paper by Z. Iofa [12], p. 120-121. What is
more, in sulfuric acid the magnitude of $\Delta E°$ is likewise somewhat smaller
than in hydrochloric acid, as we see in Table 1. Lastly, it must be thought
that the hydrogen-ion concentration also increases less rapidly in sulfuric
acid as the acid concentration is raised than is the case in hydrochloric
acid. This makes wholly understandable the highly characteristic difference
between the $v$ ($c$) curves for the velocity of the cathodic evolution of hydro-
gen in hydrochloric and sulfuric acids - an exponential function in the case
of hydrochloric acid and a nearly linear one for sulfuric acid. Moreover,
if we assume that anion adsorption has practically no effect upon the velocity
of the cathodic process in sulfuric acid, we must shift from Equation (8a) to
Equation (8b) for sulfuric acid, the latter equation containing variables
that are solely functions of the state of the solution and are unaffected by
the nature of the cathode. This makes the equality between the relative
velocities of the cathodic evolution of hydrogen at a lead cathode and the
relative dissolution rates of chromium and iron that we had observed in sul-
furic acid fully understandable as well. We therefore see that the basic set
of laws governing the variation of the rates at which chromium and iron dissolve
with the concentration of hydrochloric and sulfuric acids may be satisfactorily
explained by means of the laws governing the velocity of the cathodic evo-
lution of hydrogen in these acids. There are other facts that demand further
consideration, however. One of them is the marked difference between the
values of $\underline{W}$ for the velocities of the cathodic process and lead and mercury
electrodes and the rates at which chromium and iron dissolve (in hydrochloric
acid), referred to above. We assume that this fact may be explained in two
ways:

1) On the assumption that the factors controlling the kinetics of the
dissolution of chromium and iron are the electrode processes, we must assume
that the adsorption of an anion will have a lesser effect, for one reason or
another, upon the velocity of the cathodic evolution of hydrogen during the
dissolution of chromium and iron than when the cathodic evolution of hydro-
gen takes place at the surface of a mercury or lead cathode. In the simplest
case, this difference may be simply ascribed to a difference in the nature
of the metals themselves. We assume, however, that in addition to this
cause, another factor may play a part in this case, namely, the fact that
during the dissolution of a metal hydrogen is evolved at a continuously re-
newed surface, while in the case of a mercury or lead cathode, this evolu-
tion takes place at the surface of a metal that does not dissolve.

*Since HCl is a strong electrolyte (and chiefly because we have no other
data), we assume that the change in the concentration of the H ions is
proportional to the change in the overall acid concentration.

2) Another possible explanation of the same phenomenon is an increase in the kinetic energy of the ion-transfer process in concentrated solutions of hydrochloric acid due to conductance, i.e., an increase in the IR drop of the potential between the cathodic and anodic areas of the metal surface. Which of these two explanations is satisfactory will be considered at greater length in our forthcoming papers, which will likewise deal with the problem of the potentials of dissolving chromium and iron. Lastly, we should like to comment on still another fact. The findings reported in our papers written with Markiyevich [7] and Oranskaya [8] on the potentials of dissolving chromium and iron, the entrance of iron ions (and apparently of chromium ions as well) into solution is accompanied by appreciable anodic polarization - of the order of 0.2 to 0.26 volt. This makes it impossible to equate the kinetic energy of the anodic process to zero. This fact does not contradict the conclusions we have reached above. The behavior patterns governing the dissolution rate of a metal, provided the kinetic energies of the cathodic and anodic processes are comparable, may be handled either by means of the derived general equation by simultaneously solving the equations for the rates at which the cathode and anode processes take place, as was done in the papers by A. I. Shultin [13, 14], or by using one of these equations, say the equation for the cathodic process, and experimentally determining the potential of the dissolving metal, as has been done in the present paper. The two methods are essentially identical though there is a substantial difference between them in practice.

The first method is more complete, fundamentally speaking, since this actually allows for the behavior patterns controlling both processes, whereas in the second method the behavior patterns that govern the velocity of the anodic process are allowed for formally via the changes in the potential of the dissolving metal. Unfortunately, the first method suffers at present from the handicap that we have to know not only the behavior patterns and the equations governing the velocity of the cathodic evolution of hydrogen, but also those governing the anodic process in which the metal ions enter solution, about which much less is known at the present time. What is more, the derivation of the general equation by simultaneously solving the individual equations for the velocities of the cathodic and anodic processes is extremely complicated, as may be seen from the paper by A. Shultin; this, too, compelled us to employ the second method.

## SUMMARY

1. The feasibility of dealing with the behavior patterns governing the dissolution rates of chromium and iron in concentrated solutions of hydrochloric and sulfuric acids (ranging from 1N to 10N) on the basis of the generalized electrochemical theory has been discussed.

2. It has been shown that the $v(c)$ curves representing the variation of the chromium and iron dissolution rates with the concentration of the hydrochloric and sulfuric acids are qualitatively identical with the curves representing the variation of the velocity of the cathodic evolution of hydrogen with the concentration of the same acids.

3. The data in the papers by Z. Iofa and A. Frumkin on the hydrogen overvoltage at mercury and lead cathodes in hydrochloric and sulfuric acids and the data on the equilibrium hydrogen-electrode potential in these same solutions have been used to show that the rates of chromium and iron dissolution and the velocity of the cathodic evolution of hydrogen at a lead cathode vary identically, within the limits of experimental error, as the concentration of sulfuric acid is raised. In the case of hydrochloric acid, the velocity of the cathodic process rises faster than the rates of metal dissolution as the acid concentration is increased.

4. It has been shown that these behavior patterns are in good agreement with Z. Iofa's and A. Frumkin's theory of hydrogen overvoltage in concentrated acids.

LITERATURE CITED

[1]   Ya. Durdin, J.Gen.Chem. 21, 801 (1951).

[2]   M. Tsentnershver, Z.Phys.Chem., 137, 352 (1928).

[3]   M. Tsentnershver, Z.Phys.Chem., 122, 455 (1926).

[4]   M. Tsentnershver, Z.Phys.Chem., 141, 167 (1929)

[5]   M. Tsentnershver, Trans. of the Jubilee Mendeleev Congress, Vol. 2, 241 (1937).

[6]   M. Tsentnershver, Z.Phys.Chem., 142 (1930).

[7]   Ya. Durdin and A. Markiyevich, J.Gen.Chem. 19, 2131 (1949).*

[8]   Ya. Durdin and M. Oranskaya, J.Gen.Chem. 21, 604 (1951)**

[9]   Ya. Durdin, Sci. Rep. Leningrad State Univ., No. 40, 3 (1939).

[10] Z. Iofa,   J.   Phys.Chem. 13, 1435 (1939).

[11] Z. Iofa and A. Frumkin,    J. Phys.Chem. 18, 268 (1944).

[12] Z. Iofa,   J.   Phys.Chem. 19, 117 (1945).

[13] A. Shultin,   J.   Phys.Chem. 18, 61 (1944).

[14] A. Shultin,   J.   Phys.Chem. 18, 69 (1944).

*See Consultants Bureau English Translation page  a-605.
**See Consultants Bureau English Translation page 669.

# COMPLEX FLUORINE - TITANIUM IONS IN SOLUTION

## K. E. Kleiner

Reactions involving the decolorization of solutions of colored compounds of some metals by fluorine ions are employed, as we know, in the colorimetric determination of fluoride concentrations;  all the methods based upon these reactions have been elaborated empirically, however, so that the field of their application has been limited by the close confines of the concrete problem for which the given method of analyzing a given object has been developed.

To extend the limits of application of these methods and to secure comparative indexes for each of them, we first have to make a study of the equilibria that control the decolorizing action of fluorine ions.

The most important of these equilibria are the following:

$$MeX_m^{\alpha-m\beta} \ + \ nF^- \rightleftharpoons MeF_n^{\alpha-n} + mX^\beta \tag{I}$$

$$MeF_n^{\alpha-n} \rightleftharpoons Me^\alpha + nF^- \tag{II}$$

$$MeX_m^{\alpha-m\beta} \rightleftharpoons Me^\alpha + mX^\beta \tag{III}$$
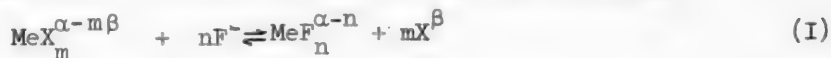
where $MeX_m^{\alpha-m\beta}$ is the colored metal compound, and $\underline{X}$ is the anion of the acid or the electrically neutral molecule (such as $H_2O_2$).

Equilibrium (I) is obviously determined not only by the activities of the reagents, but mainly by the stability relations, i.e., by the magnitudes of the instability constants of the compounds $MeF_n^{\alpha-n}$ and $MeX_m^{\alpha-m\beta}$ which are governed by Equilibria (II) and (III).

Hence, a study of Equilibria (II) and (III) must precede any endeavor  to perfect present methods of determining fluorides or of developing new ones, not merely empirically, but guided by definite laws.  The reaction between a solution of a titanium peroxide compound and fluorides is a special example of Equilibrium (I).

Numerous papers have been published on the behavior of peroxide compounds of titanium and other metals in solution [Equilibrium (III)].  They include papers by M. Rumpf [1], M. Bendig and H. Hirschmuller [2], and A.K. Babko and A.I. Volkova [3].  The last-named authors have shown that there are two compounds of titanium with hydrogen peroxide.  In acid solutions (at a pH less than 2) a colored addition product of a molecule of hydrogen peroxide and ions of titanium or titanyl are formed.  When the pH exceeds 3, a colorless salt-like compound is formed with anions of hydrogen peroxide ($HO_2^-$ or $O_2^{--}$) in the coordination sphere.  Only the colored compounds are of any use in colorimetric determination of the fluorides, of course.

These authors found that the hydrogen peroxide molecules enter into the complex ions of the colored compound in the same proportions as the titanium or titanyl ions, so that the constit.     of the complex ions may be represented by the formula $TiH_2O_2^{4+}$ or $TiOH_2O_2^{2+}$

The instability constant of this compound when dissociated is as follows:

$$Ti H_2 O_2^{4+} \rightleftharpoons Ti^{4+} + H_2O_2,$$

$$Ti O H_2 O_2^{2+} \rightleftharpoons Ti^{2+} + H_2O_2,$$
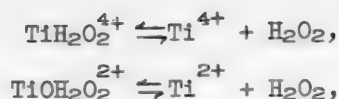
averages $1 \cdot 10^{-4}$, according to the authors cited [1, 2, 3].

Though many fluorine compounds of titanium have been described in the literature, no research has been done on the constitution and stability of these compounds in solution [Equilibrium (II) in the foregoing outline].

It is only in the paper by M. Bendig and H. Hirschmuller [2] that we can find indirect evidence of the stability of coordination compounds of titanium and fluorine; these authors determined the equilibrium constant of the reaction between a titanium compound and sodium fluoride in aqueous solution, finding $K_{equil.} = 3.5 \cdot 10^{-3}$.

In the present paper we report the results of an experimental determination of the composition and stability of fluoride complex ions of titanium, secured in an investigation of the $Ti(NO_3)_4$ [or $Ti(SO_4)_2$]-$H_2O_2$-NaF system in solutions of nitric and sulfuric acids.

All the experiments involved measurements of the optical density of the solutions in a Pulfrich photometer with a No. 7 light filter (effective wavelength 465 M$\mu$). The initial solution of titanium nitrate was prepared from the sulfate by precipitating the hydroxide three times and dissolving it in nitric acid. The titanium concentration of the solution was determined gravimetrically. The solution of sodium fluoride was prepared with the calculated quantity of the refined preparation, while the concentration of hydrogen peroxide in the original solution was determined by permanganometry. The experimental procedure and the computations were exactly like those employed in the research on fluorine coordination compounds of iron in solution [4].

The Composition of a Fluorine Coordination Compound of Titanium in Solution. The composition was determined in solutions in sulfuric and nitric acids by means of a restricted logarithmic method [5] and by the Job method [6,7].

The results obtained with the restricted logarithmic method for sulfuric-acid solutions (0.5N $H_2SO_4$) with a titanium concentration of $45.0 \cdot 10^{-3}$ mol per liter and a hydrogen-peroxide concentration of $85 \cdot 10^{-3}$ mol per liter are given in Table 1 and Fig. 1. The concentration of sodium fluoride is given in Column 2. The cell thickness was 0.5 mm.

The results obtained in our tests of other solutions are illustrated in Figs. 2 and 3.

The experimental figures obtained when the sulfuric-acid solutions were mixed (as in the Job method) are shown in Figs. 4 and 5. Curve 6 in these figures represents the change in the optical density of the solutions containing titanium, hydrogen peroxide, and sodium fluoride with variations in the ratio F/Ti, plotted along the axis of abscissas. The optical density of the solutions that contain nothing but titanium and hydrogen peroxide (in the same concentrations as for the Curves b) is represented by Curves a. The c curves were plotted from the difference between the optical densities of the a and b solutions; they indicate the progress of decolorization of the solutions (D ordinate), i.e., the change in the concentration of the fluorine coordination compound of titanium as a function of the F/Ti ratio.

These results show that the maximum decolorization of the solutions, i.e., the maximum formation of the coordination compound of titanium and fluorine, occurs at the ratio F:Ti=1:1.

16

Curves 1 and 2 in Figs. 1 and 3 have been constructed on the assumption that in the formula $TiF_n^{4-n}$, n = 1 and 2. Experimental data shown as circles in these figures agree well with the curves calculated for n = 1.



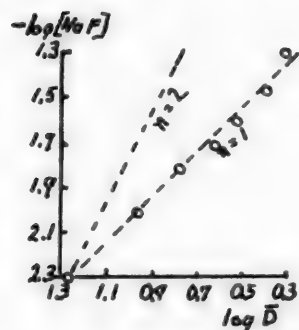Fig. 1. Sulfuric-acid solutions (0.5N $H_2SO_4$). $[Ti(SO_4)_2] = 45.0 \cdot 10^{-3}$; $[H_2O_2] = 85 \cdot 10^{-3}$ mol/liter. Cell thickness 0.5 mm.
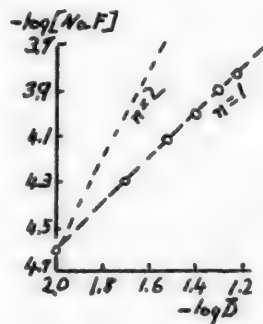
Fig. 2. Nitric-acid solutions (0.1N $HNO_3$). $[Ti(NO_3)_4] = 4.93 \cdot 10^{-3}$; $[H_2O_2] = 9.24 \cdot 10^{-3}$ mol/liter. Cell thickness 1 mm.
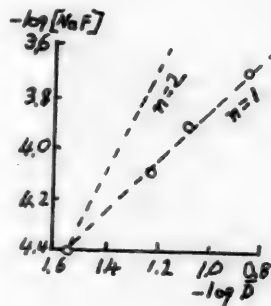
Fig. 3. Nitric-acid solutions (0.1N $HNO_3$). $[Ti(NO_3)_4] = 0.73 \cdot 10^{-3}$; $[H_2O_2]$ 0.78 $\cdot 10^{-3}$ mol/liter. Cell thickness 50 mm.

Table 1

| Test No. | NaF concentration, mol/liter | Optical density $\log \dfrac{I_o}{I}$ | Weakening of the color, $\overline{D}$ | $-\log \overline{D}$ | $-\log$ [NaF] |
|---|---|---|---|---|---|
| 1 | – | 1.04 | – | – | – |
| 2 | 0.005 | 0.985 | 0.055 | 1.26 | 2.3 |
| 3 | 0.01 | 0.93 | 0.11 | 0.96 | 2.00 |
| 4 | 0.015 | 0.87 | 0.17 | 0.77 | 1.82 |
| 5 | 0.02 | 0.80 | 0.24 | 0.62 | 1.70 |
| 6 | 0.025 | 0.74 | 0.30 | 0.52 | 1.60 |
| 7 | 0.035 | 0.63 | 0.41 | 0.39 | 1.46 |
| 8 | 0.05 | 0.55 | 0.49 | 0.31 | 1.30 |

It follows from the experiments using the restricted logarithmic method and the Job method, therefore, that at the concentrations cited above (Table 1 and Figs. 1-5) fluorine and titanium enter complex ions in a 1 : 1 ratio, so that the composition of the latter may be represented by $TiF^{3+}$ or $TiOF^+$.

The question whether a fluorine compound of titanium contains a titanium or titanyl ion cannot be answered by this investigation. Some of the experimental findings obtained in our determinations of composition and of the instability constant (vide infra) suggest that the formula $TiOF^+$ is to be preferred. By employing the functions derived by A.K. Babko [8, 9] the instability constants of more complicated ions may be calculated from the instability constants of a complex ion containing a single coordinated ion. This has been demonstrated in a number of papers, particularly in research on complex ions of fluorine with iron [4], aluminum [10], and beryllium [11]. These relationships hold good only for complex ions in which the charge on the central ion is neither screened nor neutralized (even if only partially) by other molecules or ions. A calculation for complex ions of fluorine and titanium has shown that we might expect the formation of a perceptible concentration (and at a certain composition an appreciable) concentration of complex ions with two coordinated ions of fluorine.
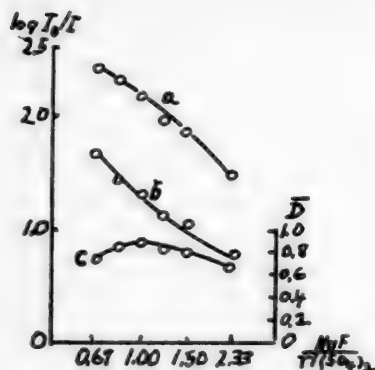
Fig. 4. Sulfuric-acid solutions (1N $H_2SO_4$). [$Ti(SO_4)_2$] + [NaF] = 0.015 mol/liter. [$H_2O_2$] = 0.075 mol/liter. Cell thickness 10 mm.
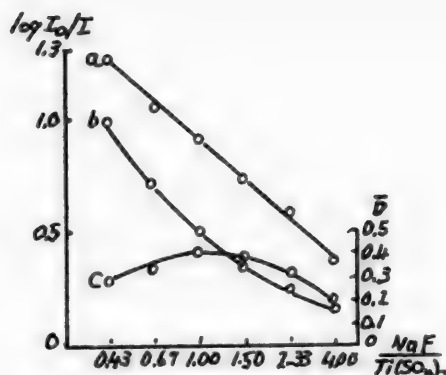


Fig. 5. Sulfuric-acid solutions (2N $H_2SO_4$). [$Ti(SO_4)_2$] + [NaF] = 0.15 mol/liter. [$H_2O_2$] = 0.26 mol/liter. Cell thickness 0.25 mm.

Inasmuch as this has not been supported experimentally, it may be concluded that the addition of a second fluorine ion involves the expenditure of considerable energy, as would follow from the functions referred to, so that we may assume that other ions than those of titanium and fluorine participate in the formation of the coordination compounds. We shall therefore prefer henceforth to represent the composition of the complex ions of fluorine and titanium by the formula $TiOF^+$, without regarding it as an established fact (this applies equally to the peroxide compound of titanium: $TiOH_2O_2^{2+}$).

In accordance with present concepts the titanium ion can move about within the oxygen octahedron inside which it is located in the space lattice of barium titanate, which is, as we know, a new Seignetto-electric. The bond between the titanium ion and the oxygen ions is partially homopolar, so that the titanium ion is displaced some 0.1 Å from the center of the octahedron toward one of the 6 adjacent oxygen ions. Inasmuch as Seignetto electric properties have been discovered in other titanates of divalent metals [12], it may be assumed that the asymmetrical arrangement of the titanium and oxygen ions is a general property of complex titanium ions containing oxygen. We may, therefore, expect that in these complex ions the bond between the titanium ion and one of oxygen ions surrounding it will be stronger than its bond with the other oxygen ions.

This bond apparently persists even in solution (titanyl ions).

### Instability Constant of Complex Ions of Fluorine and Titanium

To determine the instability constant

$$K_{TiOF^+} = \frac{[TiO^{2+}]\ [F^-]}{[TiOF^+]}$$

we ran a series of tests in 0.1N solutions of nitric acid under conditions resembling those used in determining the instability constants of $FeF^{2+}$ and other complex ions [4, 10, 11].

The reaction involved in the decolorization of a peroxide compound of Ti r. by fluorine ions is given by the underlying equilibrium:

$$TiOH_2O_2^{2+} + F^- \rightleftharpoons TiOF^+ + H_2O_2.$$
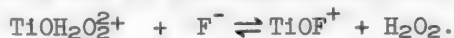
The equilibrium constant is:

$$K_{equil.} = \frac{[TiOF^+][H_2O_2]}{[TiOH_2O_2^{2+}][F^-]} = \frac{K_{TiOH_2O_2^{2+}}}{K_{TiOF^+}},$$

whence

$$K_{TiOF^+} = K_{TiOH_2O_2^{2+}} \frac{[TiOH_2O_2^{2+}][F^-]}{[TiOF^+][H_2O_2]},$$

where $K_{TiOH_2O_2^{2+}} = 1 \cdot 10^{-4}$.

The equilibrium concentration $TiOH_2O_2^{2+}$ in solutions containing a fluoride was determined experimentally from the changes in the optical density of these solutions (cols. 5, 6, and 7 in Table 2).*

The equilibrium concentrations of $TiO^{2+}$, $TiOF^+$, and $F^-$ were calculated as follows. The concentration of $TiO^{2+}$ was calculated from the expression for $K_{TiOH_2O_2^{2+}}$ after computing the equilibrium concentration of the hydrogen peroxide from $[H_2O_2]_{equil.} = [H_2O_2]_{tot.} - [TiOH_2O_2^{2+}]$.

The $TiOF^+$ concentration was calculated from the equation $[TiO(NO_3)_2] = [TiO^{2+}] + [TiOH_2O_2^{2+}] + [TiOF^+]$, while the equilibrium concentrations of the fluorine ions were calculated from the expression $[NaF] = [TiOF^+] + [HF] + [F^-]$, bearing in mind [13] that

$$K_{HF} = \frac{[H^+][F^-]}{[HF]} = 10^{-3}$$

All the experimental and computational data are listed in Table 2. All the concentrations are stated in mols or gram-ions per liter. The cell thickness was 50 mm. The instability constants of the complex ions TiOF are tabulated in Col. 11. We took the mean value of 19 tests to be $K_{TiOF^+} = 3.6 \cdot 10^{-7}$ the values ranging from $1.8 \cdot 10^{-7}$ to $4.7 \cdot 10^{-7}$.

As has been stated above, all the determinations of the instability constant were made in 0.1N solutions of nitric acid.

The equilibrium constant is:

$$TiOF^+ + H_2O_2 \rightleftharpoons TiOH_2O_2^{2+} + F^-$$

$$K_{equil.} = \frac{[TiOH_2O_2^{2+}][F^-]}{[TiOF^+][H_2O_2]} = \frac{K_{TiOF^+}}{K_{TiOH_2O_2^{2+}}} = \frac{3.6 \cdot 10^{-7}}{1 \cdot 10^{-4}} = 3.6 \cdot 10^{-3}.$$

---

*The concentration of $TiOH_2O_2^+$ ⌐ in solutions that contain no NaF may be readily computed from the equation:

$$K_{TiOH_2O_2^+} = \frac{([TiO(NO_3)_2] - [TiOH_2O_2^{2+}])([H_2O_2] - [TiOH_2O_2^{2+}])}{[TiOH_2O_2^{2+}]} = 1 \cdot 10^{-4}$$

TABLE 2

| No. | $[Ti(NO_3)_4]\cdot10^3$ | $[H_2O_2]\cdot10^5$ | $[NaF]\cdot10^5$ | $\log\frac{I_0}{I}$ | $\frac{\log\frac{I_c}{I}}{\log\frac{I_0}{I}}$ | $[TiOH_2O_2]\cdot10^5$ | $[TiO^{2+}]\cdot10^5$ | $[TiO...]\cdot10^5$ | $[F...]\cdot10^6$ | $K_{TiOF^+}\cdot10^7$ |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 |
| I | 54.56 | 95.00 | – | 0.78 | 1 | 45.39 | – | – | – | – |
| 2 | 54.56 | 95.00 | 5 | 0.73 | 0.94 | 42.67 | 8.15 | 3.74 | 0.13 | 2.8 |
| 3 | 54.56 | 95.00 | 10 | 0.68 | 0.87 | 39.49 | 7.11 | 7.96 | 0.20 | 1.8 |
| 4 | 54.56 | 95.00 | 15 | 0.66 | 0.85 | 38.58 | 6.84 | 9.14 | 0.59 | 4.4 |
| 5 | 54.56 | 95.00 | 20 | 0.63 | 0.81 | 36.76 | 6.31 | 11.49 | 0.85 | 4.7 |
| 6 | 54.56 | 95.00 | 25 | 0.60 | 0.77 | 34.95 | 5.82 | 13.79 | 1.12 | 4.7 |
| 7 | 54.56 | 95.00 | 30 | 0.57 | 0.73 | 33.13 | 5.36 | 16.07 | 1.39 | 4.6 |
| 8 | 54.56 | 139.88 | – | 0.85 | 1 | 49.14 | – | – | – | – |
| 9 | 54.56 | 139.88 | 5 | 0.81 | 0.95 | 46.68 | 5.01 | 2.87 | 0.21 | 3.7 |
| 10 | 54.56 | 139.88 | 10 | 0.77 | 0.91 | 44.72 | 4.70 | 5.14 | 0.49 | 4.4 |
| 11 | 54.56 | 139.88 | 15 | 0.71 | 0.84 | 41.28 | 4.19 | 9.09 | 0.59 | 2.7 |
| 12 | 54.56 | 139.88 | 20 | 0.69 | 0.81 | 39.80 | 3.98 | 10.78 | 0.92 | 3.4 |
| 13 | 54.56 | 139.88 | 25 | 0.66 | 0.78 | 38.33 | 3.77 | 12.46 | 1.25 | 3.8 |
| 14 | 54.56 | 139.88 | 30 | 0.64 | 0.75 | 36.86 | 3.58 | 14.12 | 1.59 | 4.0 |
| 15 | 54.56 | 139.88 | 35 | 0.60 | 0.71 | 34.88 | 3.32 | 16.36 | 1.86 | 3.8 |
| 16 | 54.56 | 186.5 | – | 0.88 | 1 | 50.81 | – | – | – | – |
| 17 | 54.56 | 186.5 | 10 | 0.78 | 0.89 | 45.22 | 3.20 | 6.14 | 0.39 | 2.0 |
| 18 | 54.56 | 186.5 | 20 | 0.73 | 0.83 | 42.17 | 2.92 | 9.47 | 1.05 | 3.2 |
| 19 | 72.75 | 97.88 | – | 1.07 | 1 | 58.13 | – | – | – | – |
| 20 | 72.75 | 97.88 | 20 | 0.87 | 0.81 | 47.08 | 9.27 | 16.40 | 0.36 | 2.0 |
| 21 | 72.75 | 97.88 | 25 | 0.85 | 0.79 | 45.92 | 8.84 | 17.99 | 0.70 | 3.4 |
| 22 | 72.75 | 97.88 | 30 | 0.81 | 0.76 | 44.18 | 8.23 | 20.34 | 0.97 | 3.9 |
| 23 | 72.75 | 97.88 | 35 | 0.78 | 0.73 | 42.43 | 7.65 | 22.67 | 1.23 | 4.2 |

Average ... $3.6\cdot10^{-7}$

This value agrees satisfactorily with the value of the constant ($K_{equil.}=3.5\cdot10^{-3}$) given by other authors [2]. This agreement serves as indirect proof that we have determined the value of the instability constant of complex ions of fluorine and titanium correctly.

## SUMMARY

1. It has been found that the composition of a complex ion of fluorine and titanium in solutions of nitric and sulfuric acids is given by the ratio F:Ti = 1:1 for concentrations of sodium fluoride ranging from $2.5\cdot10^{-5}$ to 0.12 mol per liter.

It is assumed that under these conditions titanyl ions participate in the formation of complex ions, so that the composition of the complex ions may be represented by the formula TiOF+.

2. The instability constant of the complex ions TiOF+ has been determined to be:

$$K_{TiOF^+} \frac{[TiO^{2+}][F^-]}{[TiOF^+]} = 3.6 \cdot 10^{-7}.$$

3. The equilibrium constant of $TiOF^+ + H_2O_2 \rightleftharpoons TiOH_2O_2^{2+} + F^-$ has been calculated as:

$$K_{equil.} = 3.6 \cdot 10^{-3}.$$

## LITERATURE CITED

[1] M. E. Rumpf, Ann. 8, 456 (1937).

[2] M. Bendig u. H. Hirschmuller, Z. An. Chem. 120, 385-393 (1940).

[3] A. K. Babko and A.I. Volkova, J. Gen. Chem. 21, 1949 (1951).

[4] A. K. Babko and K.E. Kleiner, J. Gen. Chem. 17, 1259 (1947).

[5] H. Bent, . C. French, J. Am. Chem. Soc., 63, 568 (1941).

[6] P. Job, Ann. 9, 113 (1928).

[7] W. Vosburgh, G. Cooper, J. Am. Chem. Soc., 63, 437 (1941).

[8] A. K. Babko, J. Gen. Chem. 15, 745 (1945).

[9] A. K. Babko, J. Gen. Chem. 16, 1549 (1946).

[10] K. E. Kleiner, J. Gen. Chem. 20, 1747 (1950).*

[11] K. E. Kleiner, J. Gen. Chem. 21, 18 (1951).

[12] G. A. Smolensky, Proc. USSR. Acad. Sci., New Series. No. 3, 405 (1950).

[13] F. Lindstrand. Uber Eisenperchlorate. Monograph (1939).

*See Consultants Bureau English Translation, page 1807.
*See Consultants Bureau English Translation, page 19.

# DOUBLE DECOMPOSITION IN THE ABSENCE OF A SOLVENT

## THE FORMATION OF COORDINATION COMPOUNDS, SOLID SOLUTIONS, AND DOUBLE DECOMPOSITION IN MOLTEN CALCIUM AND STRONTIUM FLUORIDES AND CHLORIDES.

G. A. Bukhalova and A. G. Bergman

Research on double decomposition in molten salts is even more interesting when investigating various systems possessing cations or anions in common.   In such a case we observe evolution of the diagram, as one set of ions is replaced by another.   In research on various fluoride-chloride systems of the alkali-earth elements Ca, Sr ‖ F, Cl (of the present paper); Ca, Ba ‖ F, Cl [1], and Sr, Ba ‖ F, Cl [2], for instance, we can establish the effect of various factors, such as:  the radius of the cation, the nominal thermal effect of the exchange reaction, the formation of coordination compounds, and the like, upon the double decomposition and the progressive change in the structural diagram as the system's cations are changed.

Investigation of fluoride-chloride exchange is valuable because systems consisting of fluorides and chlorides are comparatively simple, inasmuch as: 1)  they exhibit only a slight tendency to form solid solutions;  2)  their fusion curves are usually very steep and intersect sharply;  3)  up to the present time no instance has been found of the crystallization of binary or ternary heterogeneous compounds from the melts of any interhalogen reciprocal system;  and 4)  another favorable factor is the circumstance that all the halogen compounds crystallize readily and have the simplest constitutions.

We shall reserve consideration of the general nature of the Ca, Sr ‖ F,Cl system   we have investigated for our conclusions, where we consider it together with other fluoride-chloride systems of the alkali-earth metals and make a comparative analysis of these systems and discuss them.

Here we shall merely state that the diagram of the crystallization surface of the Ca, Sr ‖ F, Cl system consists of three areas of continuous series of solid solutions of fluorides of Ca and Sr, chlorides of Ca and Sr, and the compounds $CaF_2CaCl_2$ and $SrF_2 \cdot SrCl_2$ (Fig.1).

## EXPERIMENTAL

### Procedure

The research was carried out by the visual polythermal method in a platinum crucible.   Temperatures were measured with a Pt-PtRh thermocouple and a Siemens-Halske mirror galvanometer.   The melts were vigorously stirred by hand with a platinum stirrer throughout the process of slow cooling until crystals appeared in the molten mass, and, conversely, throughout the slow heating until all the crystals disappeared.   The interior of the electric

furnace was illuminated by a powerful light source to obliterate the light
emitted by the molten salts.   The initial calcium and strontium chlorides,
marked "chemically pure," were recrystallized twice from water; the calcium
and strontium fluorides were prepared by dissolving the respective carbonates
(prepared in turn from the doubly recrystallized chlorides and ammonium carbonate)
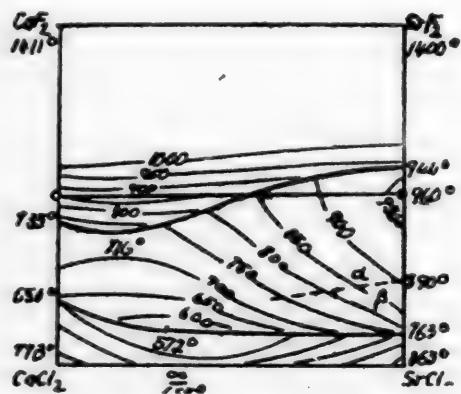in hydrofluoric acid that had been twice distilled in a platinum still.



Fig. 1. Projection of the polytherm
of the reciprocal Ca,Sr‖F,Cl
system.
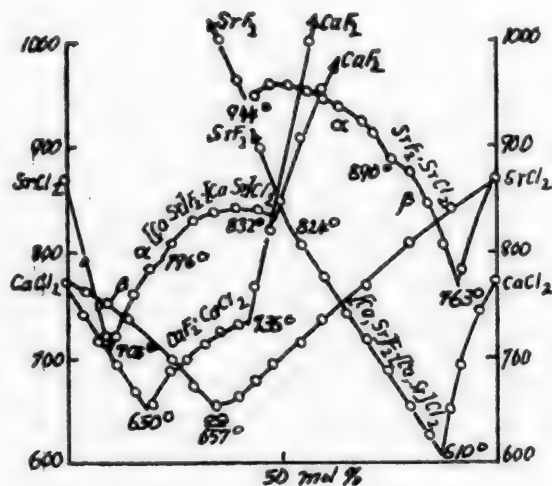


Fig. 2. Fusion curves of binary systems
and diagonal sections.

The melting points of the initial substances were as follows: CaCl$_2$-773°,
SrCl$_2$-868°, CaF$_2$-1411°, and SrF$_2$-1400° (the latter two figures were not measured).
SrCl$_2$ exhibits several homeomorphic transformations at 818, 725, and 630°, while
CaCl$_2$ has one at 608°.   These homeomorphic transformations of the SrCl$_2$ and
CaCl$_2$ salts are not manifested in the system under investigation, as their
temperatures lie below the fusion curve.

The experimental investigations were continued up to 1000°.   All
compositions are stated in molecular per cent.

## Lateral Sides-Binary Systems (Fig. 2, Table 1)

   1.   CaF$_2$-CaCl$_2$ has been investigated by Nacken [3] and Plato [4], who found that a 1 : 1 incongruent compound was formed.   We repeated their work on this system.   The eutectic point lies at 650° and 19.0% CaF$_2$, the transition point being located at 735° and 42.5% CaF$_2$.

TABLE 1

| CaF$_2$-CaCl$_2$ | | SrF$_2$-SrCl$_2$ | | SrCl$_2$-CaCl$_2$ | | SrCl$_2$-CaF$_2$ | | CaCl$_2$-SrF$_2$ | |
|---|---|---|---|---|---|---|---|---|---|
| Mol.% CaF$_2$ | t° | Mol.% SrF$_2$ | t° | Mol.% SrCl$_2$ | t° | Mol.% CaF$_2$ | t° | Mol.% SrF$_2$ | t° |
| 0 | 773 | 0 | 868 | 0 | 773 | 0 | 868 | 0 | 773 |
| 4 | 742 | 8 | 784 | 5 | 764 | 4 | 795 | 4 | 746 |
| 8 | 720 | 12 | 806 | 10 | 753 | 8 | 751 | 8 | 693 |
| 12 | 696 | 16 | 846 | 15 | 739 | 12 | 723 | 12 | 651 |
| 20 | 658 | 20 | 877 | 20 | 715 | 16 | 762 | 16 | 627 |
| 24 | 687 | 24 | 888 | 25 | 697 | 20 | 785 | 20 | 653 |
| 28 | 700 | 28 | 913 | 30 | 675 | 25 | 809 | 25 | 687 |
| 32 | 713 | 32 | 924 | 35 | 656 | 30 | 830 | 30 | 617 |
| 36 | 725 | 36 | 937 | 40 | 665 | 35 | 838 | 35 | 742 |
| 40 | 730 | 40 | 944 | 44 | 679 | 40 | 842 | 40 | 776 |
| 44 | 788 | 44 | 948 | 48 | 697 | 45 | 840 | 45 | 807 |
| 47 | 820 | 48 | 958 | 55 | 716 | 50 | 843 | 50 | 848 |
| 57 | 1000 | 52 | 958 | 60 | 736 | 55 | 907 | 55 | 900 |
| | | 56 | 950 | 70 | 770 | 60 | 954 | | |
| | | 60 | 963 | 80 | 808 | | | | |
| | | 64 | 1000 | 90 | 840 | | | | |
| | | | | 100 | 868 | | | | |

CaF$_2$-CaCl$_2$ — Intersection:
1) 650° and 19% CaF$_2$,
2) 735° and 42.5% CaF$_2$

SrF$_2$-SrCl$_2$ — Intersection:
1) 736° and 14% SrF$_2$,
2) 890° and 25.05% SrF$_2$;
3) 944° and 58% SrF$_2$

SrCl$_2$-CaCl$_2$ — Minimum: 656° and 35% SrCl$_2$

SrCl$_2$-CaF$_2$ — Intersection:
1) 708° and 10% CaF$_2$,
2) 796° and 23% CaF$_2$,
3) 832° and 49% CaF$_2$

CaCl$_2$-SrF$_2$ — Intersection:
1) 610° and 13% SrF$_2$,
2) 824° and 48% SrF$_2$

2. $SrF_2$-$SrCl_2$ has been investigated by Plato [4] and by Vinter [5], who found the congruent compound $SrF_2 \cdot SrCl_2$. Our checks of this diagram indicate that our findings do not differ essentially from those given by Plato, except for the presence of a $SrF_2 \cdot SrCl_2$ homeomorphic transformation at 890° and 25% $SrF_2$.

We have found that the melting point of $SrF_2 \cdot SrCl_2$ is 960°, with its first eutectic at 763° and 14% $SrF_2$ and its second at 944° and 58% $SrF_2$.

3. We did not do any research on $CaF_2$-$SrF_2$, owing to the high temperatures involved; it must be supposed that the curve represents continuous solid solutions with a slight minimum, since we found continuous solid and a deep minimum at 1022° in the analogous system $CaF_2$-$BaF_2$, which we did not investigate. This is supported by the fact that the difference between the ionic radii of strontium and calcium is less than between those of barium and calcium (ionic radii: Ca – 1.06 A, Sr – 1.27 A, Ba – 1.43 A).

4. $CaCl_2$-$SrCl_2$ has been investigated by several authors [6,7,8]. We have found the minimum on the continuous fusion curve for the solid solutions to lie at 656° and 35% $SrCl_2$.

The reciprocal system Ca,Sr ‖ F,Cl. Four internal and two diagonal sections were passed through this system to map the relief of the crystallization surface. They are shown in Figs. 2 and 3 and in Tables 1 and 2, their location in the system being represented in Fig. 4. It should be noticed that the Sections I, II, and III and the diagonals $CaCl_2$-$SrF_2$ and $SrCl_2$-$CaF_2$ each consist of three crystallization branches, for they intersect three series of continuous solid solutions: strontium and calcium chlorides, the anionic complex ions of strontium and calcium, and finally, strontium and calcium fluorides, denoted in the drawings as $[Ca, Sr]Cl_2$, $[Ca, Sr]F_2 \cdot$ $[Ca, Sr]Cl_2$ and $[Ca,Sr]F_2$.

The homeomorphic transformations, which are so readily observable in the $SrF_2$-$SrCl_2$ binary system along the branch representing the $SrF_2 \cdot SrCl_2$, compound, were followed by us only along Section I and the $SrCl_2$-$CaF_2$ diagonal. Section IV consists of a single branch, inasmuch as all of it lies within the region representing solid solutions.

In Fig. 5 we also show the projection of the line of joint crystallization upon the $CaCl_2$-$SrCl_2$ side, which we used to find the isothermal points on the joint crystallization lines, to fix more accurately the location of the minima on these lines, and to estimate the correspondence of the sections.

Inspecting the projection of the system's liquidus (Fig.1) and the projection of the line of joint crystallization upon the $CaCl_2$-$SrCl_2$ side (Fig.5), we conclude that the crystallization surface of the system consists of three crystallization areas, separated by two boundary curves possessing minima; they separate the crystallization area of a continuous series of solid solutions of the compounds $[Ca,Sr]F_2 \cdot [Ca,Sr]Cl_2$ from the areas representing the continuous series of solid solutions of calcium and strontium chlorides and calcium and strontium fluorides. The area of the composition square is allocated as follows among the three crystallization areas: 52.68% $[Ca,Sr] F_2$; 36.28% $[Ca,Sr]F_2 \cdot [Ca,Sr]Cl_2$; and 11.04% $[Ca,Sr]Cl_2$. It should be borne in mind that the crystallization surface of the solid solutions of the compounds $[Ca,Sr]F_2 \cdot [Ca,Sr]Cl_2$ is shown as a bent truncated cone on the projection of the liquidus diagram expanding from $CaF_2 \cdot CaCl_2$ to $SrF_2 \cdot SrCl_2$.

TABLE 2

| Section I | | Section II | | Section III | | Section IV | |
|---|---|---|---|---|---|---|---|
| 55% SrCl₂ / 45% CaCl₂ } SrF₂ | | 50% SrCl₂ / 50% CaCl₂ } CaF₂ | | 25% SrCl₂ / 75% CaCl₂ } CaF₂ | | 25% CaF₂ / 75% CaCl₂ } SrF₂·SrCl₂ | |
| Mol.% $SrF_2$ | t° | Mol.% $CaF_2$ | t° | Mol.% $CaF_2$ | t° | Mol.% $SrF_2 \cdot SrCl_2$ | t° |
| 0 | 716 | 0 | 685 | 0 | 698 | 0 | 677 |
| 2 | 690 | 3 | 642 | 4 | 666 | 10 | 685 |
| 4 | 660 | 6 | 611 | 8 | 624 | 15 | 689 |
| 6 | 643 | 9 | 576 | 12 | 595 | 20 | 698 |
| 8 | 622 | 12 | 598 | 16 | 618 | 24 | 705 |
| 10 | 644 | 17 | 644 | 20 | 656 | 28 | 711 |
| 11 | 663 | 22 | 679 | 25 | 680 | 31 | 719 |
| 17 | 725 | 27 | 699 | 30 | 696 | 34 | 725 |
| 22 | 771 | 32 | 716 | 35 | 710 | 37 | 735 |
| 27 | 806 | 37 | 732 | 40 | 733 | 40 | 747 |
| 32 | 839 | 42 | 771 | | | 44 | 763 |
| 42 | 881 | 47 | 833 | | | 48 | 778 |
| 47 | 896 | | | | | 52 | 797 |
| 52 | 906 | | | | | 60 | 830 |
| 57 | 918 | | | | | | |
| 64 | 1002 | | | | | | |

Intersection:
1) 615° and 9% SrF₂,
2) 754° and 21% SrF₂,
3) 914° and 51.5% SrF₂

Intersection:
1) 565° and 10% CaF₂,
2) 738° and 39.5% CaF₂

Intersection:
1) 581° and 12% CaF₂,
2) 716° and 39% CaF₂

The curve has no minimum



Fig. 3. Internal sections I, II, III, and IV of the system.

The isothermal lines plotted at intervals of 50° enable us to visualize the three-dimensional model of the Ca,Sr ‖ F,Cl system. It is quite obvious that in three dimensions the area of solid solutions of the compounds will be somewhat saddle-shaped.

## Conclusion

The Ca,Sr ‖ F,Cl system brings the series of investigated reciprocal systems of fluorides and chlorides of the alkali-earth metals calcium, strontium, and barium to a close.

Three factors are strikingly exhibited in these systems: the formation of coordination compounds, double decomposition, and the stability of the solid solutions.

What is most characteristic of this series of systems: Ca,Sr ‖ F,Cl (Fig.1); Sr,Ba ‖ F,Cl (Fig.6); and Ca,Ba ‖ F,Cl (Fig.7) is the formation of coordination compounds at opposite sides, giving rise to fluorides and chlorides of the alkali-earth metals.
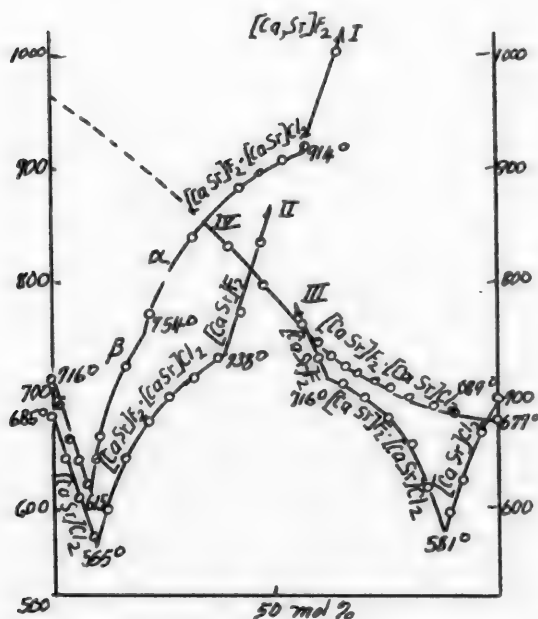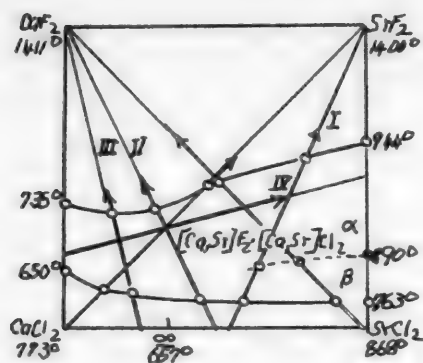
27

Fig. 4. Location of the system's internal sections.
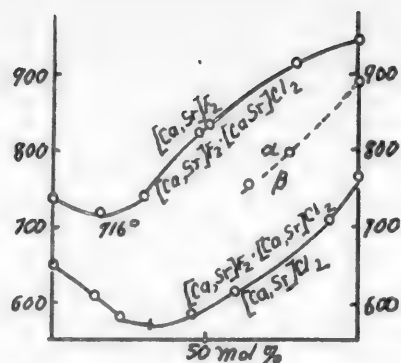


Fig. 5. Projection of the line of joint crystallization upon the CaCl₂-SrCl₂ side.

The stability of the resultant anionic coordination compounds increases with atomic number and ionic radius from calcium to barium. This is shown mainly by the melting points and heats of formation, the latter quantities were determined by N.K. Voskresenskaya and G.A. Bukhalova [10] for barium and strontium anionic coordination compounds, the data being expressed in large calories

TABLE 3

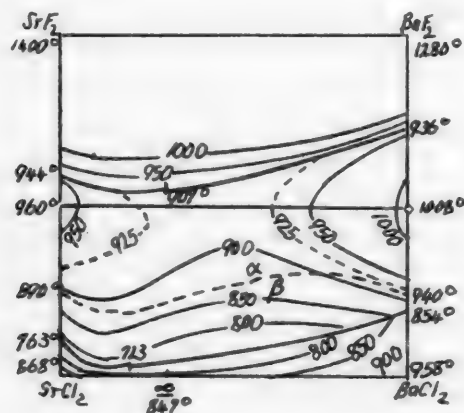| Coordination compound | Melting point | Kind of fusion | Heat of formation | |
|---|---|---|---|---|
| | | | From the Salts | From the elements |
| $BaF_2 \cdot BaCl_2$ . . . . . . . | 1008* | Congruent | 15 2 | 493 18 |
| $SrF_2 \cdot SrCl_2$ . . . . . . | 960 | Congruent . . | 4? 1 | 486 87 |
| $CaF_2 \cdot CaCl_2$ . . . . . . . | 735 | Incongruent . | - | - |



Fig. 6. Projection of the polytherm of the SrBa,∥F, Cl reciprocal system
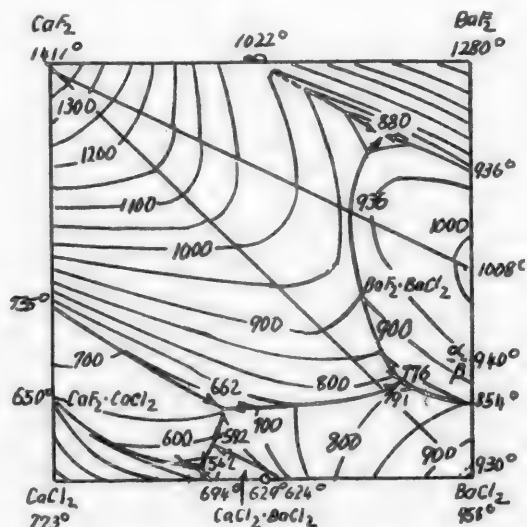


Fig. 7. Projection of the polytherm of the Ca,Ba∥F,Cl reciprocal system.

The length of the crystallization branches of the compounds in the projections of the binary systems is 55, 50, and 23%, respectively.

In the chlorides, the formation of coordination compounds has been observed only between $CaCl_2$ and $BaCl_2$ as a coordination compound congruently fusing at 629°. Nor have coordination compounds containing four different ions, i.e., coordination compounds along the stable diagonals, been found.

If compounds are formed in the binary systems that bound the composition square, it is quite natural that the compound must manifest itself in some way or another in the reciprocal system, i.e., it must have a corresponding area in the diagram that represents the crystallization surface. Then a reaction involving the formation of the compound, i.e., the reaction involved in the formation of a coordination compound, will take place in the reciprocal system, in addition to a double decomposition reaction. Experiment has shown that the reactions involved in the formation of a coordination compound and in double decomposition are antagonistic ones in reciprocal systems.

This is clearly reflected in the liquidus diagrams of the reciprocal systems. Which one of these factors, double decomposition or the formation of a coordination compound, will prevail depends upon the nominal thermal effects of the respective reactions.* It is apparent that it would be more correct to employ the free energies rather than the heats of double decomposition and of the formation of coordination compounds. But it is only for very few systems that we are able to calculate the free energies of reactions, owing to the lack of the required constants. We therefore have to resort to the simplified nominal thermochemical effect of the reactions. But, as N. K. Voskresenskaya has shown [9], this simplification is quite permissible without impairing the correctness or the significance of the calculation. We have been able to calculate the double decomposition reactions and the reactions involved in the formation of coordination compounds for the Sr,Ba ‖ F,Cl system (Fig.6), i.e., to locate the triangulating secants of the system.**
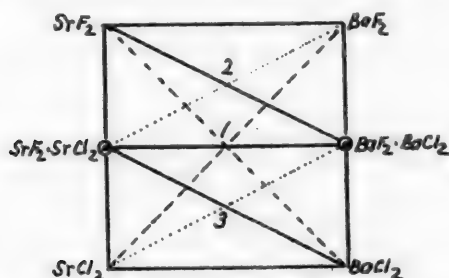


Fig. 8 Triangulation diagram of the Sr,Ba ‖ F,Cl system.

Fig. 8 is a diagrammatic sketch of the composition square of this system, with all possible sections shown. The equation for the reactions at the Point 1, where the sections of the square intersect, are represented as follows:

$$2SrCl_2+2BaF_2=2SrF_2+2BaCl_2+16.89 \text{ kcal.}$$
$$2SrF_2+2BaCl_2=SrF_2 \cdot SrCl_2+BaF_2 \cdot BaCl_2+17.79 \text{ kcal.}$$
$$2SrCl_2+2BaF_2=SrF_2 \cdot SrCl_2+BaF_2 \cdot BaCl_2+24.68 \text{ kcal.}$$
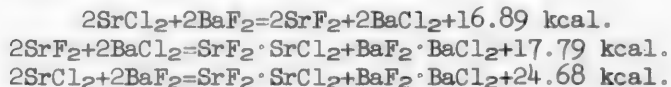
The reactions resulting in the formation of compounds entail greater thermal effects than do the double decomposition reactions. Therefore, when equimolecular proportions of

---

* The thermal effects of double decomposition reactions and the reactions involved in the formation of coordination compounds are called nominal because they are calculated from the heats of formation of the constituent salts and the compounds, which are usually given for 18-25°.

**As has been pointed out above, the heats of formation of $SrF_2 \cdot SrCl_2$ and $BaF_2 \cdot BaCl_2$ were determined by N. K. Voskresenskaya and G.A. Bukhalova, which has made it possible for us to perform the computation cited here.

29

stable and unstable pairs of components are melted together, the compounds $SrF_2 \cdot SrCl_2$ and $BaF_2 \cdot BaCl_2$ must be formed. The predominance of the reactions involved in the formation of coordination compounds is expressed geometrically by the transverse cross section $SrF_2 \cdot SrCl_2 - BaF_2 \cdot BaCl_2$ looking like a binary system, with a three-dimensional fold of maxima in the area corresponding to the solid solutions $[Sr,Ba]F_2 \cdot [Sr,Ba]Cl_2$. The diagonal section $SrF_2 - BaCl_2$, representing the double decomposition reaction is not represented geometrically in the composition diagram by anything at all.

The $SrF_2 \cdot SrCl_2 - BaF_2 \cdot BaCl_2$ section divides the composition square into two tetragons: I) $SrF_2 \cdot SrCl_2 - BaF_2 \cdot BaCl_2 - BaF_2 - SrF_2$ and II) $SrF_2 \cdot SrCl_2 - BaF_2 \cdot BaCl_2 - BaCl_2 - SrCl_2$. In turn, each of these tetragons may be regarded as an independent reciprocal system, which may be triangulated in turn. In Tetragon I the reaction at Point 2 is the controlling one:

$$2BaF_2 + SrF_2 \cdot SrCl = BaF_2 \cdot BaCl_2 + 2SrF_2 + 12.61 \text{ kcal.}$$

the reaction at Point 3 controlling in the Tetragon II:

$$2SrCl_2 + BaF_2 \cdot BaCl_2 = SrF_2 \cdot SrCl_2 + 2BaCl_2 + 4.41 \text{ kcal.}$$

We have been unable to perform a complete calculation of all the triangulating secants in the $Ca,Sr \parallel F,Cl$ and $Ca,Ba \parallel F,Cl$ systems, i.e., all the possible reactions occurring in these systems, because of the absence of data on the heat of formation of the coordination compound $CaF_2 \cdot CaCl_2$. As a result we cite merely our calculations of the nominal thermal effects of the double decomposition reaction:

$$CaCl_2 + SrF_2 = CaF_2 + SrCl_2 + 8.47 \text{ kcal.}$$
$$CaCl_2 + BaF_2 = CaF_2 + BaCl_2 + 16.98 \text{ kcal.}$$
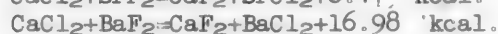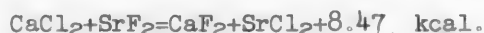
Experience in research on reciprocal systems containing coordination compounds indicates that the formation of coordination compounds usually prevails over double decomposition in reversible-reciprocal systems.

This is manifested in the liquidus diagram by the coordination compounds having well-developed areas, while the secants originating at the point in the graph that represents the composition of the coordination compounds look like binary systems, and sometimes even make it impossible to plot diagonal secants, constituting so-called adiagonal reciprocal systems.

This behavior pattern is in conformity with the fluoride-chloride systems of the alkali-earth metals. As a matter of fact, in the $Ca,Sr \parallel F,Cl$ (Fig.1) and $Sr,Ba \parallel F,Cl$ (Fig.6) systems, where the nominal thermal effects of double decomposition are 8.44 and 8.47 kcal, respectively, per molecule, and 4.22 and 4.23 kcal, respectively per equivalent, the liquidus diagram (and for the $Sr,Ba \parallel F,Cl$ system, as we have seen, calculation also) shows that the stable sections in these systems are the transverse ones that connect the points representing the compositions of two coordination compounds together; they divide the composition square into two tetragons. The extreme anticlinal folds are located along the stable secants.

In the $Ca,Ba \parallel F,Cl$ system the nominal thermal effect of the double decomposition reaction is 16.98 kcal per molecule and 8.49 kcal per equivalent. The system is an irreversible-reciprocal one, so that the areas representing the compounds $CaF_2 \cdot CaCl_2$ and $BaF_2 \cdot BaCl_2$ are not interconnected, being separated by the stable diagonal $CaF_2 - BaCl_2$.

As the liquidus diagram indicates (Fig.7), the areas of the two coordination compounds are forced back toward the sides by the ridge of the stable components. When equimolecular proportions of the coordination compounds are melted together, we get the components of the stable section:

$$CaF_2 \cdot CaCl_2 + BaF_2 \cdot BaCl_2 = 2CaF_2 + 2BaCl_2.$$

As has been stated above, one of the characteristic features of these systems: CaSr ‖ F,Cl;  Ca,Ba ‖ F,Cl;  and Sr,Ba ‖ F,Cl is their tendency to form solid solutions.

We know that one of the prerequisites for the formation of solid solutions of two constituents that possess ionic lattices is that their ionic radii be as close together as possible.  The difference between the ionic radii is 0.11 A for Sr-Ca, 0.16 A for Ba-Sr, and 0.37 A for Ba-Ca.

The large difference of 0.37 A between the ionic radii of $Ca^{++}$ and $Ba^{++}$ and the comparatively high thermochemical effect of the double decomposition reaction: 8.49 kcal per equivalent in the Ca,Ba ‖ F,Cl system hinders the formation of solid solutions of the compounds.  On the other hand, the low thermal effects of the double decomposition reactions in the Ca,Sr ‖ F,Cl and Sr,Ba ‖ F,Cl systems are unable to counteract the tendency to form solid solutions of Ca-Sr and Sr-Ba chlorides and Ca-Sr and Sr-Ba fluorides, and of the corresponding coordination compounds.

## SUMMARY

1.    The fusion diagram of the Ca,Sr ‖ F,Cl system, consisting of the three crystallization surfaces of the solid solutions:  Ca and Sr fluorides, Ca and Sr chlorides, and the two coordination compounds:  the incongruently fusing compound, $CaF_2 \cdot CaCl_2$, and the congruently fusing compound $SrF_2 \cdot SrCl_2$, has been investigated by the visual-polythermal method.

2.    The nominal thermochemical effect of the double decomposition reaction, totaling 4.23 kcal per equivalent on the $CaF_2$-$SrCl_2$ side, is unable to rupture the continuous series of solid solutions of the two coordination compounds, so that the reciprocal system's square is first divided into two tetragons, which can be triangulated still further, thus being divided into phase triangles.

3.    The results of our researches on three reciprocal systems, constituted by the fluorides and chlorides of calcium, strontium, and barium are discussed, and the laws governing the formation of coordination compounds as against double decomposition are discussed.

## LITERATURE CITED

[1]    G. A. Bukhalova and A. G. Bergman,   An adiagonal reciprocal system of the fluorides and chlorides of calcium and barium  J. Gen. Chem. 21, 1570 (1951).

[2]    A. G. Bergman and G. A. Bukhalova, J. Gen. Chem. 19, 4, 604 (1949).

[3]    Nacken. Jahrb. Miner., Geol., Pal., 1912, 545.

[4]    Plato, Z. phys. ch., 58, 350 (1907).

[5]    Vinter, Diss., Leipzig (1913).

[6]    Sandonnini, Gazz. Chim. Ital., 44, 1, 290 (1914).

[7]    Schaefer, N. Jahrb. Miner., Geo., Pal., 914, 1, 15.

[8]    Vortisch, N. Jahrb. Miner., Geol., Pal., Beilage Band, 38, 185 (1914).

[9]    N. K. Voskresenskaya, Bull. Sect. Phys-Chem. Anal. 18, 160 (1949).

[10]    N. K. Voskresenskaya and G. A. Bukhalova, J. Gen. Chem. 21, No.11 (1951).

# THE THERMAL EFFECT OF THE NATURAL AGING PROCESS IN AN
## Al-Cu ALLOY (5% Cu) AFTER HARDENING AND RECOVERY

S. M. Skuratov and N. S. Podolskaya

An alloy of Al with 5% Cu is a typical example of an alloy capable of aging (self-hardening) after being tempered.

Numerous papers have dealt with the mechanism involved in the processes that cause this alloy to harden as it ages. Historical surveys of the evolution of concepts regarding this process are to be found in the papers by S. T. Konobeyevsky [1] and D. A. Petrov [2].

The phenomenon of recovery, i.e., a sharp change in various properties of this alloy produced by a brief low-termperature annealing, has also engaged the attention of many researchers. D. A. Petrov [2] has made a thorough study of this problem. S. T. Konobeyevsky has proposed a thermodynamical theory of recovery [1]. The data in the literature and his own researches have led S. T. Konoveyevsky to conclude that even natural aging (that is, aging at room temperature) involves the separation from the supersaturated solid solution of a phase with the composition of $Al_2Cu$, very highly dispersed through the bulk of the supersaturated solid solution and in a state of metastable equilibrium with it. The phenomenon of recovery is attributed to the dissolution of this phase as the temperature is raised.

We know that the aging of alloys involves the evolution of heat. Swentoslawksi and Czochralski [3] and Czochralski, Smoluchowski, and Calus [4], for instance, have investigated the heat evolved in the aging of duraluminum. According to these authors, the process takes about 11 days, the heat evolved totaling $1.75 \pm 0.05$ cal/gram. The authors mention two more interesting facts: 1) the time curve of the evolution of heat exhibits a maximum, the location of this maximum depending upon the aging temperature; and 2) the kinetics of the evolution of heat changes markedly for even minute changes in the aging temperature (20 and 26°), though the total heat evolved (at 20 and 26°) remains the same.

An indirect criterion of the thermal effect of the aging of duraluminum may also be obtained from the Swindells and Sykes curves of the apparent heat capacity [5]. Comparing their findings for newly hardened and for aged duraluminum, these authors estimate the heat evolved in aging to approximate 1.4 cal/gram, which is rather close to the figure cited by Czochralski and his associates.

It is only in the paper by Calus and Smoluckowski [6] that we find any data on the heat evolved in the aging of binary Al-Cu alloys; stipulating that their data are merely preliminary, these authors give the following figures:

Per cent Cu in the alloys . . . . . . . . . . . . . . . 1.48   2.82   4.18
Total head evolved during aging, cal/gram . . . . . 0.057   0.092   0.290

The authors comment that the length of time during which heat is evolved increases with the percentage of copper, and that the process is concluded

within about 72 hours for 4.18% Cu.    There is nothing at all in the literature on the heat evolved during aging of alloys after recovery.

The present paper represents an attempt to study the thermal effects involved in the natural aging of an Al-Cu alloy (5% Cu) during several consecutive hardening-aging cycles and after a short period of low-temperature annealing ( recovery ).    We were interested in measuring not only the total heat evolved by the alloy, but also in securing data on the kinetics of the rate at which the heat was evolved.

Method.    A sample of the alloy (about 17 grams) was kept in a furnace at constant temperature for some time, after which it was quenched in water at room temperature for 1 minute and transferred to a calorimeter.    The calorimeter was a copper block (weighing some 500 grams), having a conical depression that exactly matched the shape of the sample.    The experiments were run under adiabatic conditions, but the aging process may be regarded as isothermal, since the temperature rise did not exceed 0.2-0.3° in any test.    The sensitivity of the calorimetric apparatus was such as to detect the evolution of 0.003 cal per gram of alloy.    No higher sensitivity was required in this case, since the reproducibility of the thermal effect of aging in various samples of the alloy was of the same order of magnitude, as will be seen below.    The heat losses of the calorimeter were carefully checked, making it possible to make measurements within 4 to 6 hours that yielded reliable results.

The fact that this calorimeter had often been employed in our laboratory for various researches and had been thoroughly tested was a guarantee that there were no appreciable systematic errors in the calometric measurements.

Some details of procedure.    The samples were quenched in water as a rule. In only one test were the samples quenched in a large copper block (weighing about 10 kg) containing a recess to fit the sample.    The temperature of the quenching bath was adjusted so as to bring the sample down to about the initial temperature of the calorimeter after 1 minute of quenching.    The large amount of water used (about 10 liters) and its vigorous stirring ensured a practically constant water temperature during quenching (±0.2°).    Quenching lasted 1 minute. Then the sample was wiped dry with filter paper as quickly as possible and transferred for 1-2 minutes to a thin-walled copper test tube  immersed in the water enveloping the calorimeter.    The temperature difference between the sample and the calorimeter was measured by a thermocouple, one junction of which was affixed to the sample, while the other was at the calorimeter's temperature. After the 1-2 minutes had elapsed, the sample was transferred to the calorimeter. This enabled correction for the heat introduced into the calorimeter by the sample owing to the difference in their temperatures.    This correction was slight, its reliability being established by a long series of special tests. In these tests we checked whether the sample introduced enough moisture into the calorimeter to affect the calorimetric measurements.    The temperature of the furnace used in the quenching tests was 520 + 2°, the samples being kept in the furnace for $1^1/_2$ hours.    Longer soaking (3 hours) affected neither the total heat evolved during aging nor the kinetics of this evolution.

In our recovery tests the conditions (furnace temperature and soaking time) were chosen so as to have the sample give off the maximum quantity of heat as it aged.    These optimum conditions (which were in full agreement with the findings of Petrov [2])proved to be:  a temperature of about 520° and a soaking time of 15 minutes.    For some of the samples the measurements of the heat evolved were paralleled by Brinell hardness tests.

The evolution of heat by the sample was observed (by the calorimeter's rise in temperature) for several hours (4-6 hours in the tests after quenching and 2-3 hours in the tests after recovery). No longer observation was required, owing to the small amount of heat evolved, the total heat evolved by the sample being determinable with adequate accuracy by extrapolation from the experimental figures.

Samples. The alloy used in these tests was prepared from an aluminum 99.7% pure and electrolytic copper. Analysis indicated that the alloy contained 4.85% copper. The alloy was pressed into a bar, from which the samples were later turned. All the samples were annealed in vacuum as follows: 24 hours at 520° cooling for 51 hours at the rate of 7.7° per hour (down to 125°), and then cooling to room temperature at the rate of 15° per hour.

## Test Results

a) Check of procedure.

Before commencing the experiments, we ran special tests to check our procedure. In these tests, instead of the alloy samples, samples made of pure aluminium, given the same preliminary treatment (heating in a furnace, quenching in water, drying, etc.), were placed in the calorimeter. These tests showed that the change in the calorimeter's temperature taking place after the sample had been placed within it was due solely to the difference between their temperatures. Heat transfer ended within 5-7 minutes, subsequent observation of the calorimeter temperature for several hours indicating that it remained quite constant.

b) Heat of aging after hardening.

The heat evolved during aging after hardening was measured at two temperatures (19.2 and 26.0°).

The results of these measurements are listed in Table 1 (for 19.2°) and Table 2 (for 26.0°).

These tables give the amount of heat evolved by 1 gram of the sample hour by hour, starting from the instant that quenching began. (The figures for the first hour have been corrected for the heat introduced into the calorimeter by the sample, owing to the difference between their temperatures.) The last column of the table gives the total heat, as found by extrapolation.

Table 1 gives the results secured in successive hardening-aging cycles for Sample 5 (5 cycles) and for Samples 8, 21 and 41 (4 cycles each) at 19.2°.

The figures in this table enable us to draw the following conclusions.

1. There is an appreciable difference among the various runs listed in the table, both in the amount of heat evolved per hour and in the total heat evolved. In 10 of the tests out of 17 (these tests being denoted by dots in the table), however, the results are very close. In these tests the total heat evolved was computed from averaged data.

2. It is worthy of note that the runs that give identical results all represent the last hardening-aging cycles for the given sample, i.e., the initial hardening-aging cycles yield unreproducible results, whereas the results become reproducible in the ensuing cycles.

3. The heat evolved in the initial cycles is lower in some instances (such as Samples 5 and 8) than in the subsequent cycles, while in other instances (Sample 21) the converse is true.

4. The greatest discrepancies are manifested by the results observed during the first hour of aging. This is quite understandable, inasmuch as some 40% of the total heat is evolved during the first hour.

## TABLE 1

Heat Evolved During Aging After Hardening the Alloy (at 19.2°).

| Sample No. | Hardening Cycles | Heat evolved by 1 gram of alloy (thousandths of a calorie) | | | | | | Total heat |
|---|---|---|---|---|---|---|---|---|
| | | After 1st Hour | After 2nd Hour | After 3rd Hour | After 4th Hour | After 5th Hour | After 6th Hour | |
| 5 | 1 | 140 | 73 | 33 | 24 | 18 | – | 340 |
| | 2° | 182 | 76 | 46 | 40 | 30 | – | 446* |
| | 3 | 216 | 106 | 70 | 52 | 36 | – | 568 |
| | 4° | 188 | 82 | 49 | 40 | – | – | 446 |
| | 5° | 195 | 76 | 52 | – | – | – | 446* |
| 8 | 1 | 123 | 69 | 48 | 36 | – | – | 387 |
| | 2 | 135 | 63 | 51 | 33 | 27 | – | 387 |
| | 3° | 168 | 78 | 45 | 33 | 27 | – | 446* |
| | 4° | 180 | 81 | 51 | 39 | – | – | 446* |
| 21 | 1 | 213 | 102 | 72 | – | – | – | 574 |
| | 2 | 213 | 102 | 66 | 48 | – | – | 552 |
| | 3° | 177 | 78 | 57 | 42 | – | – | 446* |
| | 4° | 165 | 75 | 54 | 39 | – | – | 446* |
| 41 | 1 | 169 | 92 | 59 | 45 | – | – | 499 |
| | 2 | 193 | 71 | 48 | 30 | – | – | 446* |
| | 3° | 163 | 77 | 53 | 39 | – | – | 446* |
| | 4° | 190 | 74 | 50 | 36 | 27 | 21 | 446* |
| Mean of the runs denoted by dots | | 179 | 77 | 51 | 39 | 28 | 21 | 446 |

## TABLE 2

Heat Evolved During Aging After Hardening the Alloy (at 26°).

| Sample No. | Hardening Cycles | Heat evolved by 1 gram of alloy (thousandths of a calorie) | | | | | Total heat |
|---|---|---|---|---|---|---|---|
| | | After 1st Hour | After 2nd Hour | After 3rd Hour | After 4th Hour | After 5th Hour | |
| 5 | 1 | 289 | 103 | 67 | 67 | – | 813 |
| | 2 | 283 | 109 | 94 | 64 | – | 862 |
| | 3 | 268 | 91 | 79 | 55 | – | 718 |
| | 4 | 234 | 88 | 73 | 49 | – | 718 |
| | 5 | 240 | 97 | 70 | 64 | 51 | 718 |
| | 6 | 231 | 97 | 70 | 61 | 49 | 718 |
| | 7 | 243 | 97 | 70 | 61 | – | 718 |

5. The decrease in the thermal effect follows a logarithmic curve in all the tests, beginning with the second hour of the process, i.e., beginning with the second hour the decomposition of the solid solution behaves like a first-order reaction. This enables us to extrapolate the experimental data. The

---

*Calculated from the mean of the ten runs denoted by a dot (°).

error involved in this extrapolation is insignificant, since most of the heat evolved (80-90%) has been measured experimentally.

The results secured in seven consecutive hardening-aging cycles at 26 with Sample 5 are listed in Table 2.

The following inferences may be drawn from the figures listed in this table.

1. Much more heat is evolved during aging at 26° than at 19.2°. This does not agree with Czochralski's findings [4] on duraluminum cited above. Apparently, at 26° the aging process involves much greater changes in the solid solution.

2. There is very little difference between the kinetics of the evolution of heat at 26° and at 19.2°. This also contradicts Czochralski's findings for duraluminum [4].

3. As was the case with the tests run at 19.2°, the results of the first two hardening-aging cycles at 26° differ from those secured in the subsequent cycles. On the other hand, the results of all other cycles than the first two are in good agreement.

The test in which the sample was quenched in a massive metal block exhibited a much smaller thermal effect of aging (by a factor of 8 to 10) than in the tests where the sample was quenched in water. This demonstrates the extent to which the aging process depends upon the rate of cooling of the sample during quenching. There was no use in making a study of so small a thermal effect in the calorimeter. It is quite likely that the rate at which the samples were cooled was not identical from one test to another even when they were quenched in water, this being one of the reasons for the lack of reproducibility of the experimental results.

c) Heat of aging after recovery.

In our experiments on the heat evolved during aging after recovery, we began by selecting the recovery conditions (soaking time and temperature) that would cause the sample to give off the maximum heat during aging. As we see from Table 3, these conditions (which fully agreed with Petrov's findings) were: a temperature of some 250° and a time of 15 minutes. Lower temperatures (187° in Test 2) and higher temperatures (302° in Test 1) both diminish the amount of heat evolved. Increasing the soaking time (Test 4) likewise diminishes the heat evolved, while reducing the soaking time to 6 minutes (as in Test 3) has hardly any effect.

In the next five tests (Nos. 5-9 in Table 3) the runs were made at approximately identical conditions, and their results agree fairly well. In the absence of any data, all that we could do in these cases was to estimate the total heat evolved approximately by means of extrapolation; it was found to be about 0.12 calorie per gram.

Comparison of the results of these tests, and with the figures listed in Table 1, leads to the following conclusions.

1. The heat evolved during aging is much less (by a factor of 3-4) after recovery than after hardening.

2. The evolution of heat during aging is much more quickly damped after recovery, the amount of heat evolved becoming immeasurably minute after 3-4 hours have elapsed.

3. The aging time after hardening (ranging from 1 to 5 days) has no

TABLE 3

Heat Evolved During Aging After Hardening the Alloy (at 19.2°).

| Test No. | Sample No. | Temp. of Hardening | Duration of soaking, minutes | Heat evolved by 1 g alloy (thousandths of a calorie) | | | | Notes |
|---|---|---|---|---|---|---|---|---|
| | | | | After 2nd Hour | After 3rd Hour | After 4th Hour | After 5th Hour | |
| 1 | 41 | 302° | 15 | 36 | 18 | - | - | |
| 2 | 41 | 187 | 15 | 21 | 0 | - | - | |
| 3 | 8 | 255 | 6 | 51 | 27 | - | - | |
| 4 | 41 | 248 | 30 | 39 | 12 | - | - | |
| 5 | 21 | 246 | 15 | 42 | 21 | - | - | 5 days after hardening |
| 6 | 41 | 245 | 15 | 62 | 30 | - | - | 1 |
| 7 | 8 | 242 | 15 | 75 | 36 | - | - | |
| 8 | 8 | 251 | 15 | 63 | 27 | 12 | 6 | 1 |
| 9 | 5 | 245 | 15 | 66 | 30 | - | - | 5 |

significant effect upon the kinetics or the total quantity of heat evolved during aging after recovery (Tests 8 and 9 in Table 3).

Brinell hardness tests were made of two samples (5 and 21) to prove that recovery is actually achieved under the experimental conditions we had chosen, irrespective of the aging time. In the case of Sample 5 recovery was effected 1 day after hardening, the interval being 5 days in the case of Sample 21. The results of these tests are given in Table 4.

The results of these tests, which fully agree with the data in the literature, showed that the hardness of the samples rises for several days after quenching, actually returning to value close to that for the freshly quenched state after recovery.

TABLE 4

Brinell Hardness

| | Sample 5 | Sample 21 |
|---|---|---|
| After hardening . . . . | 53.5 | 54.0 |
| 1 day later . . . . . . | 59.9 | 57.8 |
| 5 days later . . . . . | - | 67.1 |
| After recovery . . . . | 54.9 | 54.3 |

SUMMARY

1. The heat evolved during the natural aging of an Al-Cu alloy (5% Cu) after hardening becomes reproducible only after several (2-3) hardening-aging cycles.

2. The amount of heat evolved largely depends upon the aging temperature.

3. Beginning with the second hour after quenching, the heat evolved during aging drops off in accordance with a curve that approaches the logarithmic (first-order reaction).

4. The heat evolved by this alloy during aging after recovery is 3 to 4 times as small as after hardening.

5. A measurable amount of heat is evolved only during the initial stages of the aging process, this being true after recovery as well as after hardening, whereas the change in hardness continues for a much longer time.

We are sincerely grateful to Prof. M. M. Popov for his invaluable advice and guidance during this research.

## LITERATURE CITED

[1]  S. T. Konobeyevski, Jour. Exp. and Theor. Phys. 13, 185 (1843).

[2]  D. A. Petrov, Izv. Sect. Phys. Chem. Anal., USSR Acad. Sci. XVI (2), 211 (1946).

[3]  W. Swintoslawski u. J. Czochralski, Wied. Inst. Metalurgji Metaloznawstwa, 3, 59 (1936).

[4]  J. Czochralski, R. Smoluchowski u. H. Calus, loc.cit. 4, 45 (1937).

[5]  N. Swindells,  C. Sykes. Proc. Roy. Soc., (London) (A) 168, 273 (1938).

[6]  H. Calus u. R. Smoluchowski, Roczniki Chem., 18, 411 (1938).

# ANHYDROUS LITHIUM METANIOBATE

## A. V. Lapitsky

The data in the literature on lithium metaniobate are very scanty; G. B. Bucky's handbook on crystal chemistry [1] cites the refractive index of LiNbO3, while Sachariasen's paper [2] gives the values of $\underline{a}$ and $\alpha$ for the rhombohedral lattice. Neither of these sources indicates how anhydrous lithium metaniobate is obtained, nor are any physical constants given. That is why we undertook the present research.

### 1. Initial Preparations

Niobium pentoxide was prepared from tantalum-niobium residues, which contained oxides of iron, tin, titanium, silicon, and other elements, in addition to the oxides of tantalum and niobium.

In view of the fact that the initial material contained fluorides, this raw material was treated as follows. Individual 50-gram batches of this raw material were mixed with water to a pastelike consistency and then heated with 10 ml of concentrated sulfuric acid over a water bath until all the vapor of hydro-fluoric acid had been driven off. The mixture was then transferred to a beaker with distilled water, thoroughly stirred, allowed to settle, and decanted. The first wash waters were green, indicating the presence of divalent iron ions. The "residues" were washed until all iron and sulfate ions had been removed.

It should be noted that not all the iron ions could be eliminated by this method, inasmuch as the raw materials were not pulverized finely enough. The deposit was washed with a 5% solution of ammonium carbonate to speed up the elimination of the sulfate ions.

The mixture of tantalum and niobium oxides was washed on a Buchner funnel and dried at 120°, after which it was transferred to a silver cup and fused with five times its weight of a mixture of soda and caustic soda (90% $Na_2CO_3$ and 10% NaOH). After the resultant porous mass had hardened, it was transferred to a porcelain beaker with hot distilled water and heated to a boil, the traces of tin and silicon dissolving as sodium stannates and silicates. The sodium tantalates and niobates do not enter solution under these conditions, so that they can be separated from the foregoing impurities by thorough stirring and settling, followed by decantation of the supernatant solution. The sodium tantalates and niobates were dissolved in water, and the mixture of oxides was precipitated with dilute nitric acid, iron ions again appearing in the solution. The oxide mixture became a pure one after several successive decantations.

The oxides were dissolved in a calculated quantity of 40% hydrofluoric acid and the saturated solution was then treated with potassium fluoride. The solution was diluted with water until the hydrofluoric acid had a concentration of about 2% [3]. The precipitated crystals of potassium fluotantalate were filtered out, and the filtrate was evaporated until crystals of potassium hydroxofluoniobate settled out, which were recrystallized from an acid solution.

The niobium pentoxide was secured by precipitation from a solution of the potassium hydroxofluoniobate with ammonia; it was washed and suction-filtered on a Buchner funnel and then desiccated and calcined.

The lithium carbonate used as one component was chemically pure. Before use, the salt was dessicated to constant weight at 120°.

## 2. Methods of Analysis

The percentage of niobium pentoxide was determined by fusing the samples with ten times their weight of ammonium acid sulfate in a porcelain crucible, after which the alloy was treated with a 5% solution of ammonium carbonate. The niobium pentahydroxide was filtered out, dessicated, and calcined to constant weight in a porcelain crucible. The lithium oxide was determined quantitively as follows. The filtrate was evaporated to dryness in a quartz crucible and calcined to constant weight over a gas flame. The calcined residue was the lithium sulfate by weight as we know that $Li_2SO_4$ has no perceptible volatility under these conditions.

## EXPERIMENTAL

1. Preparation of anhydrous lithium metaniobate. There is no indication in the literature of any method for the preparation of anhydrous lithium metaniobate. Quiter [4] asserts that the salt $Li_5NbO_5$ is formed when lithium carbonate is reacted with niobium pentoxide. Unfortunately his paper does not indicate the method used in analyzing this salt. We produced lithium metaniobate in two ways. In the first, we borrowed the method used by Joly [5] to prepare potassium metaniobate.

1.5 g. of lithium carbonate, 5.3 g. of niobium pentoxide, and 0.52 g. of lithium fluoride were thoroughly mixed together, and the mixture was transferred to a silver crucible. The mixture was heated in a crucible furnace equiped with a thermocouple. The roasting temperature was 700°. After the crucible had cooled, its contents were treated with water to remove the lithium fluoride. After the slight excess of lithium carbonate had been removed by decantation together with the lithium fluoride, distilled water was added. This produced an extremely stable opalescent turbidity, which disappeared completely only after 10 days had elapsed. A sample of the transparent solution cautiously taken with a tiny pipet indicated the absence of the fluorine ion in the solution. The resultant salt was analyzed.

Samples: 0.1567 and 0.1944 g.

|  | Found | | Calculated for $LiNbO_3$ |
|---|---|---|---|
| $Nb_2O_5$ | 0.1421 g. or 90.08%; | 0.1749, or 89.99% | 89.90% |
| $Li_2O$ | 0.0161 g. or 10.21%; | 0.0196, or 10.24% | 10.10% |

In the second method equimolecular quantities of lithium carbonate and calcined niobium pentoxide were thoroughly comminuted in an agate mortar and then transferred to a silver crucible and heated for 4 hours to 700° in a crucible furnace. The end of the reaction was determined by the constancy of the crucible's weight. As in the previous case, the resultant salt was faintly yellow; microscopic examination disclosed minute crystals in the shape of stubby prisms. The salt was analyzed.

Samples: 0.1781 and 0.1693 g.

|  | Found | | Calculated for $LiNbO_3$ |
|---|---|---|---|
| $Nb_2O_5$ | 0.1599 g. or 89.78%; | 0.1521 g. or 89.82% | 89.90% |
| $Li_2O$ | (differences) 10.12%; | (differences) 10.18% | 10.10% |

2. **Specific gravity of anhydrous lithium metaniobate**.  The specific gravity was determined in a pyknometer, using toluene.

   Table 1 gives the specific gravity of the anhydrous lithium metaniobate prepared by both methods.

### TABLE 1

#### Specific Gravity of Anhydrous Lithium Metaniobate Prepared by Different Methods

| No. | Method of preparing anhydrous lithium metaniobate | Specific Gravity |
|---|---|---|
| 1 | Fusing together equimolecular quantities of $Li_2CO_3$, LiF and $Nb_2O_5$ . . . . . . . . . . . . . . . . . . . . . . . . . . . | 4.283 |
| 2 | Fusing together equimolecular quantities of $Li_2CO_3$ and $Nb_2O_5$ | 4.308 |

   The melting point of anhydrous lithium metaniobate was determined in a corundum crucible, using the freezing point.  Temperature was measured with a platinum-platinum/rhodium thermocouple, which had been calibrated in the following molten salts: $K_2Cr_2O_7$, NaCl and $Na_2SO_4$.  The melting point was measured in the crucible furnace, the melting point being found to be $1164 \pm 2°$.

   After the crucible had cooled, the lithium metaniobate had a clearly marked crystalline structure;  the crystals were yellow.

### SUMMARY

   1.  Anhydrous lithium metaniobate has been produced by two methods.

   2.  The melting point of anhydrous lithium metaniobate has been found to be $1164 \pm 2°$.

   3.  The specific gravity of anhydrous lithium metaniobate, as determined in a pyknometer with toluene, was 4.283-4.308, depending upon the method used in producing the salt.

### LITERATURE CITED

   [1]  G. B. Bucky.  Crystal optical analysis, Pt. 1, 80 (1944).

   [2]  Sachariasen, Skrif. Norsk. Vidensk., 4, 1 (1922);  Geoch Vert. d. Elem., 7, 97 (1926);  8, 150 (1928).

   [3]  N. A. Tananayev and G. S. Savchenko, J. Appl. Chem. 19 (10,11), 1093 (1946);  J. Appl. Chem. 20 (5), 385 (1947).

   [4]  Quiter Comptes rend., 216 (14-17) 568 (1943).

   [5]  Joly, Ann. sci. de l'ecole nor., 16, 125 (1877).

   [6]  V. I. Spitsyn, J. Gen. Chem. 19 (10), 1801 (1949).*

   *See Consultants  Bureau English Translation a-251

# HYDROXOTRIFLUOBORATES

## I. G. Ryss and M. M. Slutskaya

I. G. Ryss was the first [1] to synthesize and identify a hydroxotrifluo-
borate — a potassium salt;* previous reports by various authors on the
preparation of substances to which such a formula might be assigned were
incorrect, since the methods they employed yielded mixtures whose properties
were essentially different from those of hydroxotrifluoborates. Travers and
Malaprade [2] apparently secured a fairly pure $KBF_3OH$, but they assigned it
the incorrect formula of $K_2B_2F_8 \cdot 1\frac{1}{2}H_2O$

The synthesis of $KBF_3OH$ by the same method was described by Wamser [3]
considerably later than the publication of Ryss's paper [1].

Our investigations of the kinetics of the formation of $HBF_4$ in mixtures
of hydrofluoric and boric acids have shown that the process velocity rises
considerably with the overall solution concentration and with an increase in
the $\frac{HF}{H_3BO_3}$. ratio. We succeeded in interpreting the experimental data on the
basis of the following process mechanism [4].

When HF and $H_3BO_3$ are mixed together, boron fluoride monohydrate, $HBF_3OH$,
which behaves in solution like a strong acid, is formed nearly instantaneously.
The undissociated part of the $HBF_3OH$, which is in equilibrium with the H· and
$BF_3OH'$ ions, enters into a bimolecular reaction with the excess HF, forming
$HBF_4$ - this process may be traced as time elapses.

The synthesis of $KBF_3OH$ by adding $H_3BO_3$ to a suspension of $KHF_2$ chilled
to 0° is based upon the following considerations: the low temperature and
the low acidity of the mixture retard the conversion of the $BF_3OH'$ into $BF_4'$.
The high concentration of the K° in the resultant solution promotes the rapid
throwing down of a $KBF_3OH$ precipitate.

The excess F', formed in the reaction:

$$2KHF_2 + H_3BO_3 = KBF_3OH + KF + 2H_2O, \tag{1}$$

tends to lower the acidity of the solution; at the same time there is no need
to fear the reaction:

$$BF_3OH' + F' = BF_4' + OH', \tag{2}$$

inasmuch as the combination of the equilibrium constants for the hydrolysis of
$BF'_4$[5], the dissociation of the water, and the dissociation of HF yields an
equilibrium constant $K_2 = 6.1 \cdot 10^{-9}$. for Equation (2).

---

*There is a typographical error in the paper: 10 g. of $H_3BO_3$ is used for 25g.
of $KHF_2$. The molar ratio $KHF_2:H_3BO_3 = 1.98$ is given correctly.

## 1. Synthesis of KBF$_3$OH from KHF$_2$, HF, and H$_3$BO$_3$

It has been shown that, notwithstanding the increased acidity of the solution, KBF$_3$OH may be produced by mixing together KHF$_2$, HF, and H$_3$BO$_3$ in the quantities specified by the following equation:

$$KHF_2 + H_3BO_3 + HF = KBF_3OH + 2H_2O. \tag{3}$$

Example:  0.1 mol of KHF$_2$* was added to 4.1 g. of hot hydrofluoric acid, containing 0.1 mol of HF, weighed out in a platinum cup. After the salt had dissolved, the solution was rapidly chilled to 0° to form minute crystals, and then 0.1 mol of H$_3$BO$_3$ was added with thorough stirring. The reagents dissolved at once, a thick precipitate of KBF$_3$OH beginning to settle out of the transparent solution within 1 - 2 minutes. The whole mass solidified after standing on ice for half an hour. Suction-filtering and drying of the precipitate yielded 11.6 g. of the air-dry salt. The theoretical yield is 12.39 g, according to Equation (3).

Part of the salt was recrystallized in the 50-0° temperature range. The recrystallized product was dried, first at room temperature, and then in vacuum at 70°, 2.4 g. of the original salt yielding 1.97 g.

### Analysis of the Salt

| | Calculated | | Theoretical |
|---|---|---|---|
| Consumption of alkali with CaCl$_2$ and methyl orange present . . . . | 1.992; 1.987 | $\dfrac{\text{mols}}{123.93 \text{ g of salt}}$ | 2.000 |
| Per cent boron. . . . . . . . . . | 8.86; 8.84 | | 8.73 |

This confirms the feasibility of recrystallizing the salt mentioned above, contrary to Wamser's erroneous assertion [3]. It was found that KBF$_3$OH does not decompose when agitated for a long time with ethyl or isoamyl alcohol, nor does it dissolve in these alcohols.

### 2. Synthesis and Properties of NaBF$_3$OH

Sodium bifluoride was prepared by adding a calculated quantity of a Na$_2$CO$_3$ solution to hydrofluoric acid. The precipitate was suction-filtered, washed on a paraffin-coated Buchner filter, and dried at 100°. The product contained 99.43% and 99.09% NaHF$_2$, the average being 99.26% (determined by alkali titration). The synthesis of NaBF$_3$OH was difficult because of the high solubility of the salt, causing the BF$_3$OH' ion to undergo further transformations in solution. Moreover, the low solubility of the NaF interferes with a reduction of the solution acidity.

In our initial experiments we studied the feasibility of preparing NaHF$_2$ by a process similar to the one described by Equation (3):

$$NaHF_2 + HF + H_3BO_3 = NaBF_3OH + 2H_2O. \tag{4}$$

When 51% hydrofluoric acid, NaHF$_2$, and H$_3$BO$_3$ are mixed together at 0°, the mixture does not dissolve completely. The precipitate apparently contains some NaBF$_3$OH, inasmuch as a precipitate with the following composition: B 9.21%, acidity 15.4 milliequivalents per gram of salt,** constituting contaminated NaBF$_3$OH, was recovered after filtration of the slighly heated mixture, followed by recooling of the filtrate. In the subsequent tests, the filtrate separated without heating

---

*The potassium bifluoride, produced in the usual manner, was 99.97% pure.

** Determined in the presence of CaCl$_2$ and methyl orange.

was quickly evaporated in vacuum at room temperature, but the resultant salt samples were even more contaminated.

Purer samples were prepared by a process resembling the one described by Equation (1). Either $H_3BO_3$ was added to a mixture of $NaHF_2$ and water chilled to $0°$ or $NaHF_2$ was added to a mixture of $H_3BO_3$ and water. The molar ratio of $NaHF_2:H_3BO_3$ equaled 2. 50 to 100 ml of water was added to 1 mol of boric acid. After the reagents had been stirred together for half an hour, the small quantity of a NaF precipitate was suction-filtered out, the filtrate being either evaporated in vacuum or salted out by adding four times the volume of alcohol. The differences in the composition of the salt as prepared by the different variants employed were not significant, though the purer samples were secured when salting out was used. The mean yields of the salt approached 50% of the theoretical (when 0.05 mol of $H_3BO_3$ was used).

The composition of some of our samples (Nos. 1-6) was as follows: **

|  | 1 | 2 | 3 | 4 | 5 | 6 | Theoretical |
|---|---|---|---|---|---|---|---|
| Acidity, milliequivalents per gram of salt . . . . | 17.82 | 17.40 | 17.50 | 17.20 | 17.62 | 17.01 | 18.55 |
| Per cent boron*. . . . . . | 9.98 | 9.92 | 9.95 | 9.92 | 9.75 | 9.85 | 10.03 |

$NaBF_3OH$ is very highly soluble in water, but is not very hygroscopic (the foregoing analyses refer to the air-dry state). The salt is not decomposed when treated with ethyl alcohol, being very slightly soluble in it (about 0.3%). Its chemical properties resemble those of the $KBF_3OH$ described previously [1] and differ considerably from the properties of the substance prepared by Meerwein and Pannwitz, which they erroneously described as $NaOH·BF_3$[5].

### 3.   Decomposing $KBF_3OH$ Solutions

In our first report on the synthesis and properties of $KBF_3OH$ [1] we noted that the titratable acidity of solutions of this substance diminishes with time, because of the partial conversion of the $BF_3OH'$ into $BF_4'$. Both the acidity that can be titrated in the presence of $CaCl_2$ and methyl orange (the alkali consumption is two equivalents per gram ion of $BF_3OH$ [1]) and the percentage of boric acid measurable after the first titration is completed and after invert sugar and phenolphthalein have been added (1 equivalent of alkali per gram ion of $BF_3OH$ [1]) drop off. The decomposition of the $BF_3OH'$ follows either of these two possible patterns:

$$3BF_3OH' \rightleftharpoons 2BF_4' + H_3BO_3 + F' \tag{5}$$

or

$$2BF_3OH' \rightleftharpoons BF_2(OH)_2' + BF_4' . \tag{6}$$

Both of these equilibria are possible.

Inasmuch as $BF_3OH'$ is titrated quantitatively by using two mols of NaOH per gram ion of $BF_3OH'$, it may be said that even if $BF_2(OH)_2$ is formed in the aqueous solution, it is likewise titrated at the rate of 1 mol of NaOH per gram ion.

It is therefore impossible to compute the degree of decomposition of the $BF_3OH'$ from the decrease in the titratable acidity. We can, however, calculate

---

*As before, the boron in the $BF_4$'was not determined.

**Samples 1-3 were prepared by salting out with alcohol; samples 4-6 by evaporation.

the number of mols of $BF_4'$ formed from 1 mol of the $BF_3OH'$ initially present (this ratio is denoted below by $\underline{x}$).

Denoting the calculated consumption of alkali in the first and second titrations of the undecomposed solution by $\underline{v}_1$ and $\underline{v}_2$ and the consumption of alkali in titrating the same quantity of the partially decomposed solution of $KBF_3OH$ by $v_1'$ and $v_2'$, we can easily derive two expressions for $\underline{x}$ from the stoichiometrical proportions:

$$x = \tfrac{2}{3}\left(1- \frac{v'_1}{v_1}\right), \tag{7}$$

$$x = 1 - \frac{v'_2}{v_2}. \tag{8}^{*}$$

According to Equations (5) and (6), the maximum values that $\underline{x}$ can have are 0.667 and 0.500. The decomposition of the $KBF_3OH$ solutions with time was followed experimentally at the temperatures of 30.0, 70.0, and 90.2°, which were maintained to within $\pm 0.05°$ in an automatically regulated water thermostat.**

Solutions of three different concentrations were tested at each of the foregoing temperatures.

A weighed amount of water was kept in a flask*** within the thermostat until its temperature leveled off. Then a weighed amount of $KBF_3OH$,**** was placed in the flask and quickly dissolved by agitating the latter.

Samples taken with a pipet at equal intervals of time were emptied into a flask packed in snow (to "chill" the mixture), after which the sample was analyzed by double titration with 0.1N alkali solution. The normality of the alkali, prepared from metallic sodium, was determined against potassium biphthalate and bi-iodate, and against borax for the second titration.

The average weight of the samples taken was determined by weighing several samples specially taken for this purpose. Samples having a molality of 0.8-1, 0.33, and 0.11 weighed approximately 2, 5, and 10 grams, respectively. The results of our measurements are reproduced in Figs. 1 - 4. The values of $\underline{x}$ as calculated from the first titration (determination of "acid fluorine") are denoted by $\underline{x}_F$; those calculated from the boric-acid titration are denoted by $x_B$.

The agreement between the values of $x_F$ and $x_B$ may be regarded as satisfactory, if we remember that any error in the first titration produces an opposite error in the results of the second titration. The fluctuations in the values of $x_F$ and $x_B$ are also caused by departures in the weights of the individual samples from the mean weight. This factor was even greater in the highly concentrated solutions.

---

*In view of the fact that the salt sample used contained minute quantities of excess boric acid, a suitable small correction has been applied in the computations.

**In the series of tests run at 30° the temperature sometimes dropped to 23-24° during the night owing to power failure.

***Paraffin-coated flasks were used in the 30° tests, and rubber flasks in the tests run at 70.0 and 90.2°.

****The salt sample used in this part of the experiment contained 98.3% $KBF_3OH$ and 2.46% boric acid (partly dehydrated).
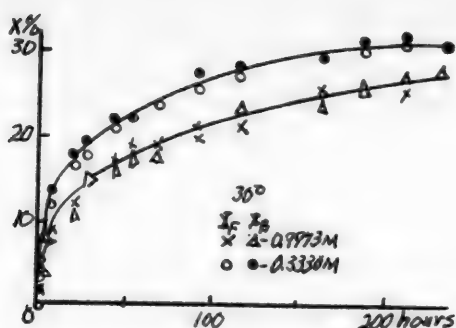
Fig.1.


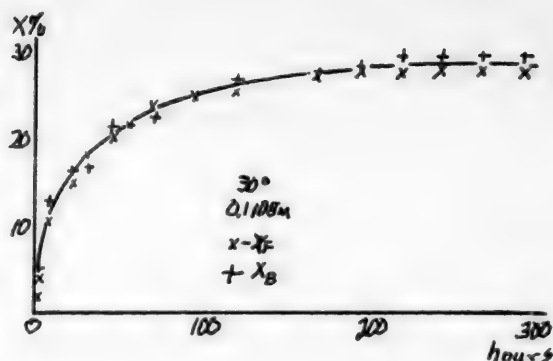
Fig.2.

At 90°, the yield of $BF_4'$ attains equilibrium within the course of $1\frac{1}{2}$ -2 hours, the state of equilibrium being reached within 5 to $6\frac{1}{2}$ hours at 70°. Owing to the high temperature coefficient of the reaction rate, the state of equilibrium was reached after 240 hours at 30°, but only in dilute solutions.

As the solution is diluted, the equilibrium yield of $BF_4'$ rises slightly, the effect of dilution being more pronounced in the 0.33 − 0.11 molality range.*

In this concentration range the process described by Equation (5), involving an increase in the number of dissolved particles, apparently acquires greater importance.

A rise in temperature produces a slight increase in the equilibrium yield of $BF_4'$, which is more perceptible in a more diluted solution. This indicates that the formation of $BF_4'$ is a very slightly endothermic process.

The heat of reaction [5] may be calculated by summation of the heats of the partial reactions:

$$2BF_3OH' + 2HF_{\alpha q} = 2BF_4' + 2H_2O + 6.46 \text{ kcal. [6]}$$

$$H^\cdot + BF_3OH' + 2H_2O = H_3BO_{3\alpha q} + 3HF_{\alpha q} - 13.74 \text{ kcal. [7]}$$

$$HF_{\alpha q} = H^\cdot + F' + 3.05 \text{ kcal. [8]}$$

$$3BF_3OH' + 2BF_4' = H_3BO_{3\alpha q} + F' - 4.2 \text{ kcal.}$$

In the reaction involved in the dissolution of boric acid in hydrofluoric acid, about 4.6 kcal. are evolved per mol of HF, i.e., somewhat more than when HF reacts with the $BF_3OH'$. If the hydroxyl groups in the boric acid are replaced by fluorine gradually, it is probable that each successive substitution stage involves the liberation of less heat, and the heat of the reaction $BF_2(OH)'_2$ + $HF_{\alpha q} = BF_3OH' + H_2O$ must be less than 4.6 kcal. Then the heat absorbed in Reaction (6) must be less than 4.6 − 3.2 = 1.4 kcal, so that this equilibrium must be even less dependent upon temperature than was the case for the equilibrium (5).

When we compare the curves of $\underline{x} = \underline{f}$ (time) for the various solution concentrations, we find that the formation of $BF_4'$ in $KBF_3OH$ solutions is a process the order of which is somewhat less than unity. Endeavors to have the shape of each of the curves represent an equation of a reversible first-order process for each course taken by the reactions** were unsuccessful — as $\underline{x}$ increased, the formation of $BF_4'$ decreased faster than the above hypothesis presupposed. The reaction is apparently highly complex, the direct reaction

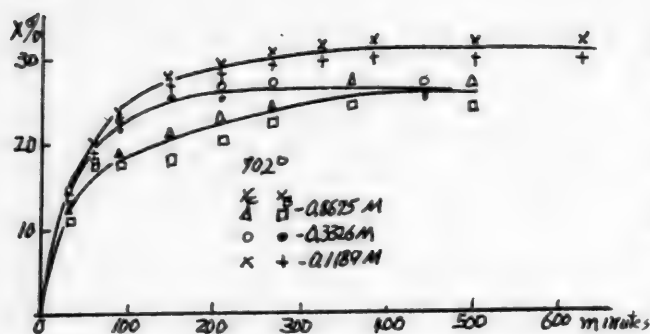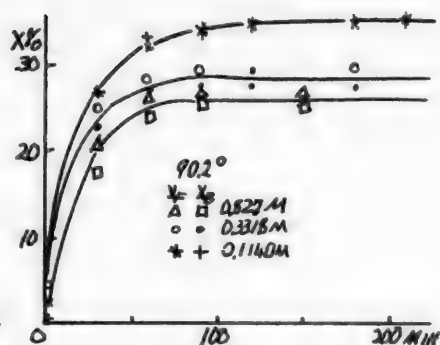* See Footnotes next page.    ** See footnote next page.

49

Fig 3.



Fig. 4.

being slowed down by its own products (the increase in pH, due to an accumulation of fluorine ions in the solution, may play a part).

## 4. The Solubility of KBF₃OH

The sample of salt used in this section of our investigation contained 8.82% B. The consumption of alkali in $CaCl_2$ and methyl orange was 1.970 mol per 123.93 g. of the salt.

5.5 g. of $KBF_3OH$ was mixed with 30 ml of water in a paraffin-coated test tube, immersed in a Dewar flask filled with ice. The paraffin-coated stirrer was driven at 60 rpm by a Warren fractional hp. motor. Samples of the solution were taken at regular intervals, and separated from the precipitate at 0°. The results of our analysis of these samples are given in Table 1.

TABLE 1

Saturation of Water With KBF₃OH at 0°.

| Saturation time, hours | 0 | 2 | 19 | 43 | 67 | 91 |
|---|---|---|---|---|---|---|
| $v_1$ ml/gram (0.0947 N NaOH) . . | 8.83 | 10.87 | 10.87 | 10.88 | 10.86 | 10.84 |
| $v_2$ ml/gram (0.0933 N NaOH) . . | 4.77 | 5.92 | 6.03 | 6.03 | 6.06 | 6.05 |

The maximum consumption of alkali (at 43 hours) is equivalent to a $KBF_3OH$ ''solubility'' of 6.4% (according to $v_1$) or 6.55% (according to $v_2$)***

The results of our solubility measurements at 45.1° are given in Table 2. Here the test tube was immersed in a thermostat, the temperature of which was kept constant within ± 0.03°. 10 g. of water was used for 10 g. of the salt.

---

*The figures for the solution of 0.3330 molality at 30° do not tally with the behavior patterns outlined above. It may be that an error crept into this series (solution concentration ), causing a systematic exaggeration of several per cent in the computed values of $x$

**As has been shown previously [9], the decomposition of $BF_4'$ in an aqueous solution is described by an equation for a first-order reaction.

***Applying a correction for the excess boric acid in the salt and assuming that all of it is dissolved.

TABLE 2

Saturation of Water With $KBF_3OH$ at $45.1°$

| Saturation time, minutes | 30 | 70 | 140 | 205 | 265 | 325 | 385 |
|---|---|---|---|---|---|---|---|
| $\underline{v}_1$ ml/gram | 53.77 | 55.53 | 53.78 | 60.22 | 56.73 | 57.09 | 57.38 |
| $\underline{v}_2$ ml/gram | 29.1 | 30.56 | 32.62 | 34.25 | 32.16 | 32.13 | 31.99 |

The maximum consumption of alkali (after 205 minutes) is equivalent to a $KBF_3OH$ "solubility" of 35.3% (according to $\underline{v}_1$) or 37.1% (according to $\underline{v}_2$ applying a correction for the excess boric acid contained in the salt).

It should be emphasized that the gradual decomposition of $KBF_3OH$ solutions (see the preceding section of this paper) makes it impossible to determine the true solubility of the salt. The formation of $KBF_4$ must lower the solubility of the $KBF_3OH$ slightly. The accumulation of the freely soluble $KBF_2(OH)_2$ must reduce the solubility of the $KBF_3OH$ considerably, but since the former salt is likewise titrated by the alkali, the measured solubility of $KBF_3OH$ is too high. Lastly, the accumulation of boric acid must tend to overstate the "solubility" of the $KBF_3OH$ as computed from $\underline{v}_2$.

Still, the calculated values of the "solubility" : 6.4% at $0°$, 11% at $14°$ [1], and 35.3% at $45.1°$ are evidence that the hydroxotrifluoborate is much more soluble than potassium tetrafluoborate.

## SUMMARY

1. A new method of synthesizing potassium hydroxotrifluoborate, by reacting a mixture of potassium bifluoride and hydrofluoric acid with boric acid, is described.

2. The synthesis of sodium hydroxotrifluoborate is described. This salt is very freely soluble in water. Its other chemical properties resemble those of the potassium salt.

3. The tetrafluoborate is formed in solutions of the hydroxotrifluoborate, a state of equilibrium between the two being reached that depends but little upon the temperature or the concentration of the solution.

4. The rate at which $BF_4'$ is formed drops slightly as the initial concentration of $BF_3OH'$ is increased and rises sharply with rising temperature.

5. The solubility of $KBF_3OH$ is 6.4% and 35.3% at $0°$ and $45.1°$, respectively.

## LITERATURE CITED

[1] I. G. Ryss, Proc. USSR Acad. Sci. 54, 327 (1946).
[2] A. Travers, L. Malaprade, Bl. Soc. Chim., 47, 788 (1930).
[3] C. Wamser, J. Am. Chem. Soc., 70, 1209 (1946).
[4] I. G. Ryss and M. M. Slutskaya, J. Gen. Chem. 19, 1827* (1949); I. G. Ryss, J. Gen. Chem. 19,** 1836 (1949).
[5] H. Meerwein, W. Pannwitz, J. pr. Ch., 141, 123 (1934).
[6] I. G. Ryss, Proc USSR Acad. Sci. 52, 421 (1946); I. G. Ryss, M. M. Slutskaya, and S.D. Palevskaya, Jour. Phys. Chem. 22, 1322 (1948).
[7] J. Thomsen, System. Durchfuhr. thermochem. Untersuchungen, Stuttgart (1906).
[8] W.A. Roth, Lieb. Ann., 542, 36 (1939).
[9] I. G. Ryss and M. M. Slutskaya, Jour. Phys. Chem. 21, 549 (1947).

Chair of General Chemistry,
March 10, 1950           Dnepropetrovsk Metallurgical Institute.

*See C.B. English translation, page a-281.
**See C.B. English translation, page a-291.

# I. A. KABLUKOV'S AND D. P. KONOVALOV'S RESEARCHES ON THE ELECTROCHEMISTRY OF NONAQUEOUS SOLUTIONS

D. A. Pospekhov

The present article sets forth several comments on the significance of the researches of I. A. Kablukov [2,3] and of D. P. Konovalov [5-8] on electrically conducting nonaqueous solutions. Notwithstanding the rather wide knowledge of these researches, insufficient light has been shed upon their importance. We shall endeavor to do so in connection with the Nernst-Thomson rule.

As we know, that rule was set forth almost simultaneously by Thomson [28] and Nernst [24,25]. The substance of the rule is that the attractive force between the ions of the dissolved substance varies inversely with the dielectric constant of the solvent. This gave rise to the concept of the dissociating power of a solvent. Nernst indicated the parallelism between the dielectric constant and the conductance of a solution. Subsequently, Walden [30,31] derived the expression $\varepsilon_1 \sqrt[3]{v_1} = \varepsilon_2 \sqrt{v_2} = \text{const.}$ ( $\varepsilon$ = dielectric constant, and $\underline{v}$ = dilution), for tetraethylammonium iodide in a large number of solvents, the expression being valid for equal degrees of dissociation.

The Nernst-Thomson rule and the cited researches of Walden were criticized by various authors, principally V. A. Plotnikov [10-14] and M. I. Usanovich [18-20]. Plotnikov [13] asserted that Walden's expression was highly approximate for a large number of cases: in the given solvent pair $N(C_2H_5)_4I$ may have identical degrees of dissociation at equal dilutions, but the ratio of the values of $\varepsilon$ does not equal unity for these solvents, lying rather between 1.2 and 1.5; the same salt may exhibit degrees of dissociation that differ by a factor of 1.5 in two solutions with approximately equal values of $\varepsilon$ at equal dilutions.

In stating his rule, Thomson cited no concrete examples, while Nernst illustrated the rule with a table on p. 49.

In support of the rule, Nernst cited the results previously obtained by Kablukov [3] in his researches on solutions of hydrogen chloride in various organic solvents, noting the parallelism between conductance and dielectric constant, the conductance being extremely low in benzene, xylene, and hexane ( $\varepsilon$ = 2.2 - 2.4), appreciably higher in ether ( $\varepsilon$ = 4.4), and much higher in various alcohols, being highest in methanol ( $\varepsilon$ = 33.7) and dropping progressively in ethyl, propyl, and isobutyl alcohols, the $\varepsilon$ being 25, 22, and 19, respectively. At the time the $\varepsilon$ of isoamyl alcohol was unknown, so that Nernst made no mention of Kablukov's findings on the solution of HCl in that substance. The $\varepsilon$ of isoamyl alcohol is 15,

| Medium | Dielectric Constant | Electrolytic dissociation |
|---|---|---|
| Gas space . . . . . . | 1.0 | Not measurable at ordinary temperatures |
| Benzene . . . . . . . | 2.3 | Extremely small, but definitely established conductivity, indicating traces of dissociation |
| Ethyl alcohol . . . . | 25 | Clearly perceptible |
| Water . . . . . . . . | 80 | Very strong |

<u>i.e.</u>, the lowest in this series, which agrees with the minimum conductance of HCl observed by Kablukov. In addition to Kablukov's researches, Nernst also mentions the later paper by Wakeman [29] who reported that the dissociation of acids dissolved in water decreased as alcohol was added, adding that this fact was a result of the decrease in the $\varepsilon$ of the medium. As we see, Kablukov's findings were, at bottom, the main foundation for the rule in question. No mention has been made of this up to the present time. Plotnikov, for example, cites [13] some excerpts from Nernst's paper [25] without saying a word about Kablukov's findings in this connection. In his discussion of the Nernst-Thomson rule, Usanovich [18-20] likewise fails to indicate the significance of Kablukov's researches in this connection. In Walden's comprehensive work on the electrochemistry of nonaqueous solutions [30], the author often refers to this research of Kablukov's on various occasions, but does not mention the part played by the latter in the establishment of the rule.

Plotnikov found various instances of rather high conductance in solvents with very low dielectric constants [10-13] [solutions in bromine ( $\varepsilon = 3.18$), benzene ( $\varepsilon = 2.3$), ether ( $\varepsilon = 4.4$), and chloroform ( $\varepsilon = 5.0$)]. This was of fundamental importance in establishing the limits within which the Nernst-Thomson rule was applicable. Some authors (Plotnikov, Usanovich, and Fredenhagen) reject this rule entirely because of these and similar facts [10-14, 18-20, 22, 27].

With the passage of time, Walden's opinions of the role of the dielectric constant in conducting solutions changed considerably, influenced by the researches of the authors cited [10-14, 18-20, 22, 27] as well as by his own experiments [32,33] that postdated his initial researches [30,31]. His lecture at the Mendeleev Jubilee Congress in 1934 [1], where he acknowledged the ability of media with extremely small values of $\varepsilon$ to dissociate dissolved substances into ions completely, is highly characteristic in this connection. Plotnikov made special mention of this point [14], asserting that " ..... when Walden began his research, he spoke of nothing but the dissociating power; but now he has reached the conclusion that many <u>substances become</u> electrolytes when interacted with suitable solvents. I have always regarded electrochemical conformity as the most important factor in conductance phenomena."

Nernst, in his repeatedly republished <u>Theoretical Chemistry</u>, comments on the Nernst-Thomson rule without saying a word about the fact of appreciable conductance in media with low values of $\varepsilon$ .

We shall show that the facts set forth in the papers by D. P. Konovalov, which were published in 1892-1893 [5-8], should have been taken into account in the period that immediately followed the establishment of the Nernst-Thomson rule (1893). Konovalov investigated the conductance of binary systems consisting of aromatic amines and aliphatic acids, finding appreciable conductance existing in systems consisting of aniline as one component and acetic, propionic, or butyric acid as the other [5,8]. It should be noted that the dielectric

constants of these acids were unknown in 1893 [16], so that Nernst, in
his commentaries on the rule he had propounded  [24,25], made
the (incorrect) assumption that these constants must lie between the values of
the respective constants for the alcohols and water.  Thus the absence of any
mention of Konovalov's researches in the cited paper by Nernst was quite
natural.  The dielectric constants of acetic, propionic, and butyric acids
were reported by Jahn and Moller [23] in 1894 (in a paper published in the same
issue of the journal as that of Nernst [25]) to be 6.4 (at 20°), 3.14 (at 19°),
and 2.9 (at 16°), respectively.

   This made appropriate comment on the Nernst-Thomson inescapably necessary,
inasmuch as the facts established by Konovalov were evidence of the existence
of appreciable conductance in solutions possessing low dielectric constants,
contrary to the rule.  Although the literature on the rule eventually became
rather extensive, no light has been shed on the significance of Konovalov's
researches for the rule down to the present time.  Plotnikov [13], in a special
discussion of Konovalov's views regarding the cause of the conductance of
solutions, makes no mention of the latter's researches dealing with the Nernst-
Thomson rule.  In Waldens's monograph on the electrochemistry of nonaqueous
solutions [30], he refers repeatedly to Konovalov's researches, but not in
connection with this rule.

   Konovalov's investigations [5-8] have been checked experimentally and
discussed repeatedly from various standpoints [4,9,13,17,21,26].  The
conductance of the aniline-acetic acid system has recently been measured by
Cherbov [21], Trifonov and Cherbov [17], Klochko and Chanukvadze [4], and
Naumova [9], their findings being close to those secured by Konovalov.  There
is, therefore, no ground for doubting Konovalov's findings on the binary
systems consisting of aniline and propionic or butyric acid.  Let us say at
once that the conductance of systems containing aniline decreases in the
following order:  acetic acid — propionic acid — butyric acid, i.e., parallel
to the decrease in their dielectric constants.  We reproduce some of Konovalov's
data for a temperature of 21°, the aniline concentration being always given
in per cent by weight (first figure) and in molar per cent (second figure)
[5,8].

   Aniline — acetic acid system: 4.00 (2.62)% $x = 0.267 \cdot 10^{-4}$; 20.60
(14.95)% $x = 2.705 \cdot 10^{-3}$;  35.01 (26.06)% $x = 2.47 \cdot 10^{-3}$.

   Aniline — propionic acid system:  14.32 (11.74)% $x = 0.66 \cdot 10^{-4}$;
22.30 (18.59)% $x = 0.36 \cdot 10^{-3}$.

   Aniline — butyric acid system:  15.65 (14.95)% $x = 0.6 \cdot 10^{-5}$;  27.10
(26.02)% $x = 0.7 \cdot 10^{-4}$.

   The minimum concentrations cited above for the systems containing
propionic and butyric acids agree with the figures given by Konovalov.

   The first paper by Plotnikov, whose findings he opposed to the Nernst-
Thomson rule, goes back to 1902 [10,15] (solutions of $AlBr_3$ in $C_2H_5Br$).
At 15 mol.% of $AlBr_3$ $x = 0.85 \cdot 10^{-3}$, at 24.7 mol.% $x = 2.09 \cdot 10^{-3}$.  This
paper was described by Patten [27] as a striking demonstration of the error
of the Nernst-Thomson rule, since the $\varepsilon$ of ethyl bromide is 8.9.

   The Konovalov figures cited above indicate that they can be used even
more successfully than the figures cited by Plotnikov in opposition to
the Nernst-Thomson rule, since they were published at a much earlier date
and refer to solvents with lower dielectric constants.

   The fact that the concentration of aniline in the systems containing
propionic and butyric acids is relatively high in no way diminishes the

merits of Konovalov's figures as evidence against the Nernst-Thomson rule, since the dielectric constant of aniline is low (7.12 at 16°), as Jahn and Moller established in the same paper in which they gave the values of $\varepsilon$ for the acids mentioned above [23].

Subsequently Plotnikov found a number of other instances of high conductance in solvents possessing low dielectric constants. In most of these cases the values observed by Plotnikov were of the same order of magnitude as in the papers by Konovalov. For example, when the percentage of phospheric acid in ether ranged from 12.7 to 54.1% by weight, it had a $\underline{x}$ ranging from $0.736 \cdot 10^{-5}$ to $0.838 \cdot 10^{-3}$ [12]. Concentrations of $SbBr_3$ in bromine, ranging from 7.1 to 47.7% by weight, had values of $\underline{x}$ ranging from $0.14 \cdot 10^{-6} - 98 \cdot 10^{-6}$. Solutions of the coordination compound of dimethylpyrone with trichloroacetic acid, $C_7H_8O_2 \cdot 2CCl_3COOH$, in benzene, chloroform, and ethyl bromide exhibited conductance ranging from $10^{-4}$ to $10^{-3}$ (in $C_2H_5Br$ $\varepsilon = 8.9$, i.e., the largest value in this series even to $10^{-2}$) [11,13]. $PBr_5$ in bromine exhibited a value of $\alpha$ ranging from $0.87 \cdot 10^{-8}$ at 3.31% by weight to $5.34 \cdot 10^{-2}$ at 36.0% by weight [15]. These and similar findings enabled Plotnikov to take a stand in 1908 [13] against the Nernst-Thomson rule as not being in agreement with actuality.

To sum up, it may be asserted that the part played by I. A. Kablukov and D. P. Konovalov in the evolution of one of the major hypotheses of the electro-chemistry of solutions has been considerably minimized.

## LITERATURE CITED

[1] P. Walden, Trans. Mendeleev Jubilee Congress I, 516-522. Moscow-Leningrad (1936).

[2] I. Kablukov. Modern solution theories (of van't Hoff and Arrhenius) and the doctrine of chemical equilibrium, 134. Moscow (1891).

[3] I. Kablukov Z. Phys. Chem. 4, 429 (1889).

[4] M. A. Klochko and O. P. Chanukvadze, Bull. USSR Acad. Sci., Div.Chem.Sci., 1938, 987.

[5] D. P. Konovalov, Jour. Russ. Chem. Soc. 24, 440 (1892).

[6] D. P. Konovalov, J. Russ. Chem. Soc. 25, 211 (1893).

[7] D. P. Konovalov, J. Russ. Chem. Soc. 25, 192 (1893)

[8] D. P. Konovalov, Lieb Ann., 49, 742 (1893).

[9] A. S. Naumova, J. Gen. Chem. 19, 1216* (1949).

[10] V. A. Plotnikov, J. Russ. Chem. Soc. 34, 466 (1902).

[11] V. A. Plotnikov, J. Russ. Chem. Soc. 37, 318 (1904).

[12] V. A. Plotnikov, J. Russ. Chem. Soc. 38, 1282 (1905).

[13] V. A. Plotnikov, Researches on the Electrochemestry of Nonaqueous Solutions, 10-19, 25-27, 49-57. Kiev (1908).

[14] V. A. Plotnikov, Coll. Rep. First All-Union Conf. on Nonaqueous Solutions, 29, 33, 34, 45. Kiev (1935).

[15] V. A. Plotnikov, Proc. Inst. Chem. Ukrain. Acad. Sci. 5, 272-275 (1938).

[16] Technical Encyclopedia. Handbook 4, 277-284 Moscow (1930).

*See C.B. English translation, p. 1211.

[17]  A. N. Trifonov and S. I. Cherbov, Bull. Perm. Biolog. Inst. 6, 247 (1928).

[18]  M. I. Usanovich, J. Gen. Chem. 2, 443 (1932).

[19]  M. I. Usanovich, Sympos. on 35th Anniv. of Scientific Career of Academician B. A. Plotnikov, 70-79 Kiev. (1936).

[20]  M. I. Usanovich, J. Phys. Chem. 6, 924 (1935).

[21]  S. I. Cherbov, Bull. Inst. Phys. Chem. Anal. 3, 459 (1926).

[22]  Fredenhagen Z. Phys. Chem. 152, 321 (1931).

[23]  J. Jahn, Moller, Z. Phys. Chem. 13, 393 (1894).

[24]  Nernst, Gottinger Nachr. 12 (1893).

[25]  Nernst, Z. Phys. Chem. 13, 531 (1894).

[26]  Patten, J. Phys. Chem. 6, 554 (1902).

[27]  Patten, J. Phys. Chem. 8, 548 (1904).

[28]  J. J. Thomson, Phil. Mag. 36, 320 (1893).

[29]  Wakeman, Z. Phys. Chem. 11, 49 (1893).

[30]  Walden, Elektrochemie der nichtwassrig. Losungen, Leipzig (1924).

[31]  Walden, Z. Phys. Chem. 54, 228 (1905).

[32]  Walden Z. Phys. Chem. 147, 30 (1930).

[33]  Walden, Z. Phys. Chem. 165, 259 (1933).

# THE PHYSICO-CHEMICAL ANALYSIS OF THE BINARY SYSTEMS OF UREA AND THE PHENOLS

## I. CONDUCTANCE, VISCOSITY, AND DENSITY

D. E. Dionisyev and N. Z. Rudenko

Research on the following systems: urea — pyrocatechol, urea — resorcinol, and urea — hydroquinone by the thermal method of physico-chemical analysis has shown [1] that urea enters into a 1:1 compound with these diatomic phenols.

As we know, the presence of chemical interaction is often manifested on the curves of other system properties, this being particularly true of rational systems. In irrational systems the compounds that form are partially dissociated at the melting point, while in the liquid phase they may be dissociated completely and not exhibit chemical action on the curves of other properties. Although the thermal method must be regarded as the principal method of physico-chemical analysis, it must be supplemented by other methods [2]. Only a comparison of the different properties of a system, investigated at different temperatures, can furnish a reliable answer concerning the composition and stability of a chemical compound. With these considerations in mind, we made an investigation of the density, viscosity, and conductance of the binary systems cited above, besides investigating the density, viscosity, and conductance of the urea — phenol system.

Conductance was measured by the Kohlrausch method in a closed vessel with smooth platinum electrodes. An audio-frequency vacuum-tube oscillator connected to a booster was used as a source of current. To increase the precision of measurement the current minimum was fed into a two-stage vacuum-tube amplifier, from which it was fed into the indicator (high-impedance headphones and a "magic eye").

Internal friction was measured in a viscosimeter of the closed type.

We measured the density of the system mainly in order to compute the internal friction, for in most cases viscosity by itself can hardly furnish an indication of the nature of the interaction between the system's components [3]. Density was measured with a Regnault pyknometer. The temperature fluctuations in the oil thermostat employed did not exceed 0.15°.

### The Urea — Phenol System

The fusibility of the urea — phenol system has been investigated by Kreman [4] and by Philip [5]. They found a compound with the composition of $CO(NH_2)_2 \cdot 2C_6H_5OH$ and a m.p. of 60.6°. The compound was highly dissociated; one of its eutectics had the same melting point as the compound itself (60.6°, its composition being 33.4 molar per cent of urea). We checked this section of the fusibility curve and confirmed these findings.

In our research we used phenol with a b.p. of 181° and a m.p. of 41°·, the m.p. of the urea was 133°.

## Viscosity

The viscosity was measured at 120 and 135°. The results of our measurements are listed in Table 1, the viscosity being represented in Fig. 1 as a function of the concentration, expressed in molar per cent.

As we see in Fig. 1, the viscosity isotherms are curves that are slightly concave upward.

TABLE 1

| No. | Mol. % $CO(NH_2)_2$ | Viscosity $\eta \cdot 10^3$ 120° | 135° | No. | Mol. % $CO(NH_2)_2$ | Viscosity $\eta \cdot 10^3$ 120° | 135° |
|---|---|---|---|---|---|---|---|
| 1 | 90.00 | – | 23.6 | 7 | 45.00 | 17.8 | 13.9 |
| 2 | 80.00 | 26.3 | 21.0 | 8 | 40.00 | 16.6 | 13.0 |
| 3 | 70.00 | 23.9 | 19.1 | 9 | 35.00 | 15.6 | 12.3 |
| 4 | 60.00 | 21.6 | 17.1 | 10 | 30.00 | 14.2 | 11.2 |
| 5 | 55.00 | 20.5 | 16.1 | 11 | 20.00 | 11.9 | 9.6 |
| 6 | 50.00 | 19.0 | 15.0 | 12 | 10.00 | 10.2 | 8.2 |

Isotherms of this sort are evidence of the absence of any chemical interaction between the system components. Nor does the calculated absolute temperature coefficient of viscosity in the 120-135° range (Table 2 and Fig.2) give any indication of chemical interaction in the system.

TABLE 2

| No. | Mol. % $CO(NH_2)_2$ | $\alpha_\eta$ (135-120°) |
|---|---|---|
| 1 | 80.00 | 35.4 |
| 2 | 70.00 | 32.0 |
| 3 | 60.00 | 30.0 |
| 4 | 55.00 | 29.3 |
| 5 | 50.00 | 26.7 |
| 6 | 45.00 | 26.0 |
| 7 | 40.00 | 24.0 |
| 8 | 35.00 | 22.0 |
| 9 | 30.00 | 20.0 |
| 10 | 20.00 | 15.3 |

TABLE 3

| No. | Mol. % $CO(NH_2)_2$ | Density 120° | 135° |
|---|---|---|---|
| 1 | 90.00 | – | 1.1947 |
| 2 | 80.00 | 1.1751 | 1.1653 |
| 3 | 70.00 | 1.1360 | 1.1254 |
| 4 | 60.00 | 1.1148 | 1.1051 |
| 5 | 50.00 | 1.0776 | 1.0680 |
| 6 | 40.00 | 1.0522 | 1.0412 |
| 7 | 30.00 | 1.0350 | 1.0247 |
| 8 | 20.00 | 1.0103 | 1.0050 |
| 9 | 10.00 | 0.9974 | 0.9898 |

The density was measured at the same temperatures (Table 3). The curves showing the density as a function of the concentration are slightly concave upward, (Fig. 3).

## Conductance

The conductance was likewise measured at 120 and 135°. The measurement results are tabulated in Table 4, the curves of conductance as a function of composition being reproduced in Fig. 4. In this system the conductance drops from that of phenol to that of urea along a curve that is concave upward. M. I. Usanovich [6] was the first one to observe conductance isotherms of this shape for systems in which the components did not interact chemically. It was later found, however, that conductance isotherms of this sort are encountered in systems in which chemical interaction does occur [7], as exhibited in the curve of the "derived" conductance $\underline{x}\eta$ and the curve of the conductance temperature
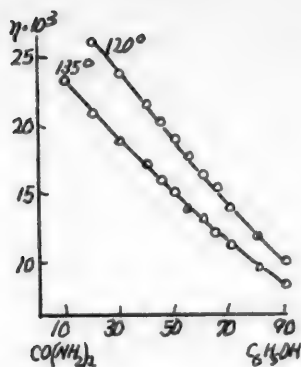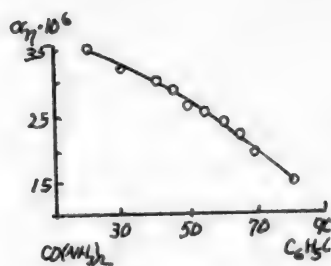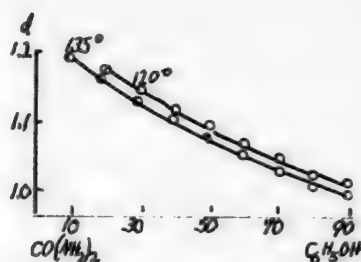
Fig.1        Fig.2        Fig.3

coefficient $\alpha_{\underline{x}}$.

We calculated the temperature coefficient of conductance within the 135-120° temperature range. The results of the calculation are given in Table 5, while the functions of concentration are plotted in Fig.5. We also corrected the conductance for viscosity (Table 6 and Fig.6). Both the temperature coefficient curve and that of the corrected conductance are smooth, without any singular points (maxima, minima, or points of inflection).

TABLE 4

| No. | Mol. % $CO(NH_2)_2$ | Conductance $\underline{x} \cdot 10^5$ | | No. | Mol. % $CO(NH_2)_2$ | Conductance $\underline{x} \cdot 10^5$ | |
|-----|------|------|------|-----|------|------|------|
| | | 120° | 135° | | | 120° | 135° |
| 1 | 90.00 | - | 22.8 | 7 | 45.00 | 4.5 | 8.0 |
| 2 | 80.00 | 14.2 | 19.5 | 8 | 40.00 | 3.5 | 6.2 |
| 3 | 70.00 | 11.4 | 16.1 | 9 | 35.00 | 2.8 | 5.1 |
| 4 | 60.00 | 8.7 | 12.8 | 10 | 30.00 | 2.4 | 4.14 |
| 5 | 55.00 | 7.3 | 11.0 | 11 | 20.00 | 0.5 | 2.2 |
| 6 | 50.00 | 6.0 | 9.7 | | | | |



Fig.4        Fig.5        Fig.6

61
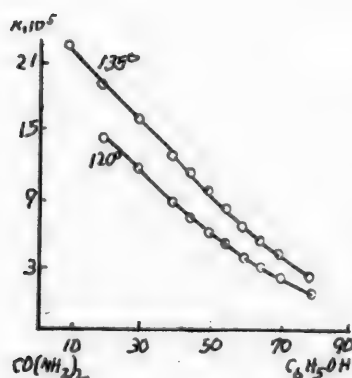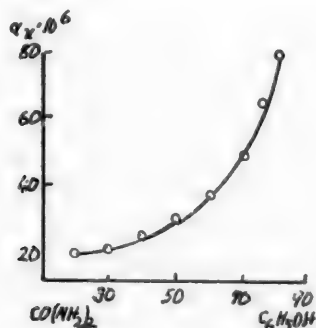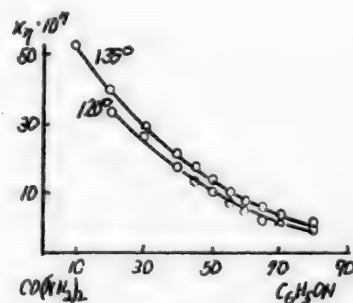
|  | TABLE 5 |  |  |
| --- | --- | --- | --- |

| No. | Mol. % $CO(NH_2)_2$ | $\alpha_x \cdot 10^6$ $(135\text{-}120°)$ |
| --- | --- | --- |
| 1 | 80.00 | 20.9 |
| 2 | 70.00 | 22.8 |
| 3 | 60.00 | 25.3 |
| 4 | 50.00 | 31.8 |
| 5 | 40.00 | 37.7 |
| 6 | 30.00 | 50.0 |
| 7 | 25.00 | 66.0 |
| 8 | 20.00 | 82.0 |

TABLE 6

| No. | Mol. % $CO(NH_2)_2$ | $\bar{x}\eta \cdot 10^7$ | |
| --- | --- | --- | --- |
| | | 120° | 135° |
| 1 | 90.00 | – | 53.9 |
| 2 | 80.00 | 37.4 | 41.0 |
| 3 | 70.00 | 27.2 | 30.8 |
| 4 | 60.00 | 18.8 | 21.9 |
| 5 | 55.00 | 15.0 | 17.7 |
| 6 | 50.00 | 11.4 | 14.5 |
| 7 | 45.00 | 8.38 | 11.1 |
| 8 | 40.00 | 5.8 | 8.11 |
| 9 | 35.00 | 4.36 | 6.28 |
| 10 | 30.00 | 3.4 | 4.56 |
| 11 | 20.00 | 1.14 | 2.11 |

## The Urea — Pyrocatechol System

A thermal investigation of the system disclosed the existence of a compound, $CO(NH_2)_2 \cdot o\text{-}C_6H_4(OH)_2$ with a m.p. of 91° [1].

Pyrocatechol with a m.p. of 105° was used in this research.

The viscosity was measured at 120 and 135°, the results being listed in Table 7 and the curves of viscosity as a function of concentration being plotted in Fig.7.

TABLE 7

| No. | Mol.% $CO(NH_2)_2$ | Viscosity $\cdot 10^3$ | | No. | Mol.% $CO(NH_2)_2$ | Viscosity $\cdot 10^3$ | |
| --- | --- | --- | --- | --- | --- | --- | --- |
| | | 120° | 135° | | | 120° | 135° |
| 1 | 90.00 | – | 27.6 | 8 | 50.00 | 38.4 | 29.8 |
| 2 | 80.00 | 36.1 | 28.4 | 9 | 47.50 | 37.9 | 29.4 |
| 3 | 70.00 | 37.2 | 29.3 | 10 | 45.00 | 37.3 | 28.8 |
| 4 | 60.00 | 38.2 | 30.0 | 11 | 40.00 | 35.9 | 27.8 |
| 5 | 57.50 | 38.4 | 30.1 | 12 | 30.00 | 31.6 | 24.4 |
| 6 | 55.00 | 38.5 | 30.2 | 13 | 20.00 | 27.8 | 21.0 |
| 7 | 52.50 | 38.6 | 30.0 | 14 | 10.00 | 25.0 | 19.2 |

The viscosity curves exhibit a clearly visible maximum at 52.5 mol.% of urea for the 120° isotherm, which is displaced to about 55 mol.% of urea and is somewhat less peaked on the 135° isotherm. As we know [2], the presence of maxima on the viscosity isotherms is evidence of the existence of chemical interaction between the components.

The temperature coefficient of viscosity very often indicates the nature of the interaction within the system and the composition of the resulting compound. We calculated the temperature coefficient of viscosity (Table 8). The coefficient is plotted as a function of composition in Fig. 8. The temperature coefficient curve has a sharp maximum, located at 50 mol.% of urea.

The density isotherms for 120 and 135° (Table 9 and Fig.9) are straight lines. This form of density isotherms is evidence of the existence of chemical interaction rather than of its absence.

| No. | Mol. % $CO(NH_2)_2$ | $\alpha_x \cdot 10^6$ $(135-120°)$ |
|---|---|---|
| 1 | 80.00 | 51.5 |
| 2 | 70.00 | 52.7 |
| 3 | 60.00 | 54.6 |
| 4 | 55.00 | 55.3 |
| 5 | 50.00 | 58.7 |
| 6 | 45.00 | 56.5 |
| 7 | 40.00 | 55.2 |
| 8 | 30.00 | 48.0 |
| 9 | 20.00 | 45.3 |

TABLE 8

| No. | Mol. % $CO(NH_2)_2$ | Density | |
|---|---|---|---|
| | | 120° | 135° |
| 1 | 90.00 | - | 1.2210 |
| 2 | 80.00 | 1.2267 | 1.2128 |
| 3 | 70.00 | 1.2160 | 1.2090 |
| 4 | 60.00 | 1.2080 | 1.1928 |
| 5 | 50.00 | 1.1971 | 1.1840 |
| 6 | 40.00 | 1.1878 | 1.1740 |
| 7 | 30.00 | 1.1785 | 1.1684 |
| 8 | 20.00 | 1.1690 | 1.1561 |
| 9 | 10.00 | 1.1594 | 1.1482 |

TABLE 9

## Conductance

The conductance was measured at the same temperatures as were used for the viscosity. The measurements are listed in Table 10, the conductance being plotted as a function of concentration in Fig.10. As we see in Fig.10, the conductance isotherm for 120° has a minimum at about 52 mol.% of urea, while one of the isotherm's branches has a maximum at 35 mol. % of urea. As the temperature is raised, the minimum persists, being shifted toward the component with higher conductance, while the maximum vanishes. The shape of the conductance isotherms is evidence of chemical interaction. Assuming that the conductance of this system is greatly affected by the viscosity and wishing to follow the conductance curve without the action of viscosity, we eliminated the latter factor.

TABLE 10

| No. | Mol. % $CO(NH_2)_2$ | Conductance x $\cdot 10^5$ | | No. | Mol. % $CO(NH_2)_2$ | Conductance x $\cdot 10^5$ | |
|---|---|---|---|---|---|---|---|
| | | 120° | 135° | | | 120° | 135° |
| 1 | 90.00 | - | 26.0 | 8 | 50.00 | 14.5 | 22.3 |
| 2 | 80.00 | 16.6 | 25.4 | 9 | 47.50 | 14.6 | 22.0 |
| 3 | 70.00 | 15.8 | 24.1 | 10 | 45.00 | 15.0 | 21.8 |
| 4 | 60.00 | 15.1 | 22.6 | 11 | 40.00 | 15.4 | 21.6 |
| 5 | 57.50 | 14.4 | 22.4 | 12 | 30.00 | 15.6 | 20.5 |
| 6 | 55.00 | 14.6 | 22.2 | 13 | 20.00 | 14.0 | 18.8 |
| 7 | 52.50 | 14.4 | 22.3 | 14 | 10.00 | 11.8 | 16.3 |

The results of our calculation of the corrected conductance are given in Table 11, the curves being plotted in Fig.11. The maximum has vanished on the curves of the "derived" conductance, a point of inflection appearing in the region of the minimum, at 50 mol. % of urea. The curve (Fig.12) of the calculated temperature coefficient of conductance for the temperature range of 135-120° is rather complicated, with a maximum at 50 mol. % of urea.

## Evaluation of Results

The viscosity isotherms of the urea — phenol system, and the curves of the temperature coefficient of viscosity, are quite smooth and slightly concave upward; the isotherms of conductance and density have the same shape, as do the curves of the "corrected" conductance and of the temperature coefficient of conductance. The curves of these properties thus do not reflect any chemical interaction within the system, and do not bear out the existence of the compounds
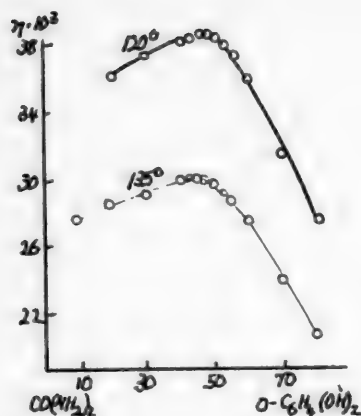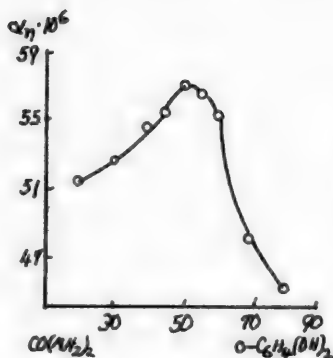
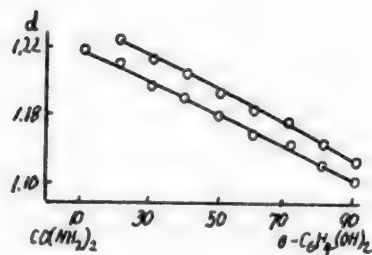$$CO(NH_2)_2 \cdot 2C_6H_5OH,$$

Fig.7.                    Fig.8.                    Fig.9.

|            | TABLE 11 |          |          |
| ---------- | -------- | -------- | -------- |

| No. | Mol. %<br>$CO(NH_2)_2$ | $\underline{x\eta \cdot 10^7}$ 120° | 135° |
| --- | ---------------------- | ----------------------------------- | ---- |
| 1   | 80.00                  | 60.0                                | 72.0 |
| 2   | 70.00                  | 58.9                                | 70.5 |
| 3   | 60.00                  | 57.5                                | 68.0 |
| 4   | 55.00                  | 56.3                                | 66.9 |
| 5   | 52.50                  | 55.3                                | 66.9 |
| 6   | 50.00                  | 55.5                                | 66.5 |
| 7   | 45.00                  | 55.5                                | 63.5 |
| 8   | 40.00                  | 55.1                                | 60.0 |
| 9   | 30.00                  | 49.3                                | 50.0 |
| 10  | 20.00                  | 39.0                                | 39.5 |

|            | TABLE 12 |          |
| ---------- | -------- | -------- |

| No. | Mol. %<br>$CO(NH_2)_2$ | $\underline{\alpha x \cdot 10^6}$ (135-120°) |
| --- | ---------------------- | -------------------------------------------- |
| 1   | 80.00                  | 28.0                                         |
| 2   | 70.00                  | 27.8                                         |
| 3   | 60.00                  | 26.6                                         |
| 4   | 50.00                  | 28.3                                         |
| 5   | 40.00                  | 22.3                                         |
| 6   | 30.00                  | 18.1                                         |
| 7   | 20.00                  | 19.5                                         |
| 8   | 10.00                  | 23.5                                         |

indicated by the fusibility method.  It may be that this compound, which is dissociated rather appreciably even at its melting point, dissociates completely in the  liquid phase.

In the urea — pyrocatechol system, the viscosity isotherms exhibit an irrational maximum that is shifted toward the more highly viscous urea.  The conductance isotherms have a minimum at 50 mol. % of urea, while those of the "corrected" conductance exhibit a point of inflection in this region.  The curves of the temperature coefficients of viscosity and of conductance have maxima located exactly at 50 mol. % of urea.

The shapes of the curves of these properties are indisputable evidence of chemical interaction within the system.  The maximum and the points of inflection at 50 mol. % of urea are evidence of a compound with a composition of $CO(NH_2)_2$ $o$-$C_6H_4(OH)_2$,     i.e., the same compound that was found by the fusibility method.

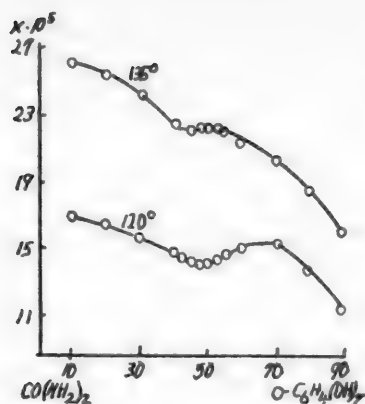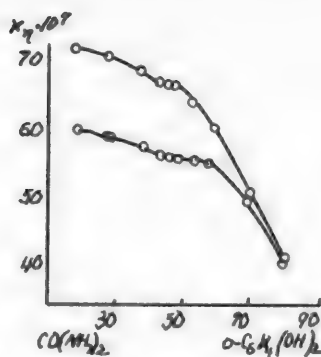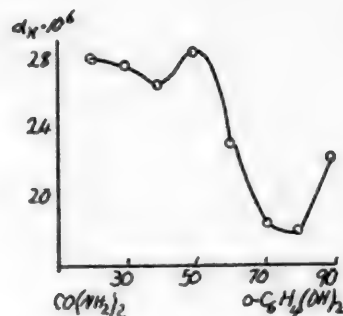Fig. 10.                Fig. 11.                Fig. 12.

## SUMMARY

1. The viscosity, density, and conductance of the urea – phenol and urea – pyrocatechol systems have been determined at 120 and 135°.

2. No chemical interaction has been detected in the urea – phenol system.

3. The components have been found to interact in the urea – pyrocatechol system, and the existence of the equimolecular compound $CO(NH_2)_2 \cdot o\text{-}C_6H_4(OH)_2$, has been proven.

## LITERATURE CITED

[1]  I. Timmermans, Les solutions concentrees. Paris, VI, 522 (1936).

[2]  N. S. Kurnakov. Introduction to physico-chemical analysis. Moscow-Leningrad (1940).

[3]  E. V. Biron, J. Russ. Chem. Soc. 41, 569 (1909);  45, 1985 and 2002 (1913).

[4]  Kremann u. Rodenis, Monatsh., 27, 125 (1906).

[5]  Philip, J. Chem. Soc., London, 83, 814 (1903).

[6]  M. I. Usanovich, J. Phys. Chem. 9, 923 (1935).

[7]  V. V. Udovenko and R. P. Airapetova, J. Gen. Chem. 17, 425 (1947).

[8]  A. S. Naumova, J. Gen. Chem. 19, 1228*(1949).

*See C.B. English translation, p. 1223.

# THE PHYSICO-CHEMICAL ANALYSIS OF THE BINARY SYSTEMS OF UREA AND THE PHENOLS

## II. CONDUCTANCE, VISCOSITY, AND DENSITY

D. E. Dionisyev and N. Z. Rudenko

In our preceding paper [1] we showed that urea and phenol do not interact in the liquid phase and that the curves of the properties studied do not confirm the existence of the compound $CO(NH_2)_2 \cdot 2C_6H_5OH$ established by the fusibility method. In the urea — catechol system, however, the formation of the compound $CO(NH_2)_2 \cdot o\text{-}C_6H_4(OH)_2$, is corroborated. Pursuing our investigation, we have made a study of the conductance, viscosity, and density of the following systems: urea — resorcinol and urea — hydroquinone.

As in our previous paper [1], we measured the conductance in a closed vessel with smooth platinum electrodes, the internal friction in a closed Ostwald viscosimeter, and the density in a Regnault pyknometer.

### The Urea — Resorcinol System

Viscosity was measured at 120 and 135°. The measurement results are listed in Table 1, while the curves of viscosity as a function of concentration, expressed in molar per cent, are plotted in Fig. 1.

TABLE 1

| No. | Mol. % $CO(NH_2)_2$ | Viscosity $\eta \cdot 10^3$ | | No. | Mol. % $CO(NH_2)_2$ | Viscosity $\eta \cdot 10^3$ | |
|-----|-----|-----|-----|-----|-----|-----|-----|
| | | 120° | 135° | | | 120° | 135° |
| 1 | 90 | – | 29.1 | 7 | 45 | 60.2 | 40.8 |
| 2 | 80 | 39.0 | 31.0 | 8 | 40 | 60.1 | 41.2 |
| 3 | 70 | 46.6 | 34.8 | 9 | 35 | 60.0 | 41.2 |
| 4 | 60 | 52.9 | 38.0 | 10 | 30 | 59.7 | 41.0 |
| 5 | 55 | 57.5 | 38.9 | 11 | 20 | 59.0 | 40.5 |
| 6 | 50 | 59.9 | 39.9 | 12 | 10 | 58.5 | 39.8 |

As we see in Fig.1. the viscosity isotherms rise steeply from the less viscous urea, passing through a moderate maximum and dropping along an almost straight line to the viscosity of resorcinol. On the 120° isotherm the maximum is located at about 45 mol. % of urea, shifting toward the more viscous component as the temperature is raised. The shape of the viscosity isotherms indicate that chemical interaction between the components takes place within the system. The absolute temperature coefficient of viscosity has been calculated (Table 2). Its curve (Fig.2) exhibits a maximum located at 50 mol. % of urea.
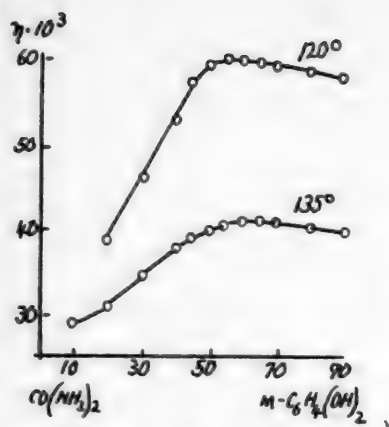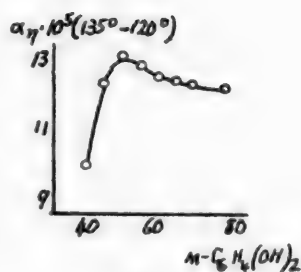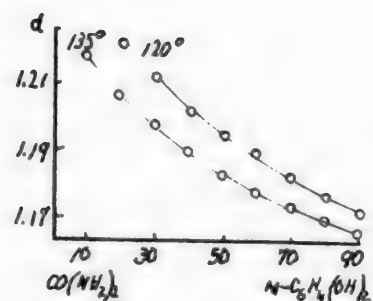
Fig. 1.



Fig. 2.



Fig. 3.

TABLE 2

| No. | Mol. %<br>$CO(NH_2)_2$ | Temperature<br>coefficient of<br>Viscosity $\alpha \cdot 10^5$ |
|---|---|---|
| 1 | 80 | 5.33 |
| 2 | 70 | 7.87 |
| 3 | 60 | 9.25 |
| 4 | 55 | 12.4 |
| 5 | 50 | 13.3 |
| 6 | 45 | 12.9 |
| 7 | 40 | 12.6 |
| 8 | 35 | 12.5 |
| 9 | 30 | 12.4 |
| 10 | 20 | 12.3 |

TABLE 3

| No. | Mol. %<br>$CO(NH_2)_2$ | Density | |
|---|---|---|---|
| | | 120° | 135° |
| 1 | 90 | – | 1.2178 |
| 2 | 80 | 1.221 | 1.2063 |
| 3 | 70 | 1.2115 | 1.1976 |
| 4 | 60 | 1.2021 | 1.1900 |
| 5 | 50 | 1.1948 | 1.1840 |
| 6 | 40 | 1.189 | 1.1791 |
| 7 | 30 | 1.1783 | 1.1756 |
| 8 | 20 | 1.1740 | 1.1712 |
| 9 | 10 | 1.1735 | 1.1650 |

The curves plotted from the data in Fig. 3, showing the density as a function of the composition at 120 and 135° are reproduced in Fig. 3. They are slightly concave upward.
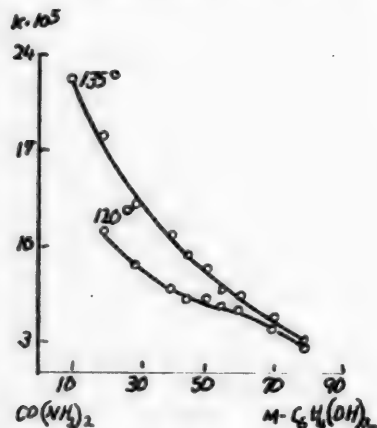


Fig. 4.
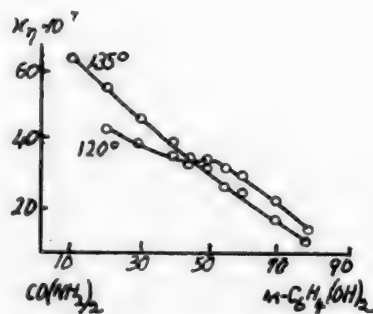


Fig. 5.

## Conductance

Conductance was measured at the same temperatures as those used in the viscosity measurements. The conductance measurements are listed in Table 4, while the curves showing the variation of conductance with composition are reproduced in Fig. 4. As we see in Fig. 4, the conductance isotherm at 120° drops     from the value of conductance for urea and exhibits a point of

Table 4

| No. | Mol. % $CO(NH_2)_2$ | Conductance $\chi \cdot 10^5$ | | No. | Mol. % $CO(NH_2)_2$ | Conductance $\chi \cdot 10^5$ | |
|---|---|---|---|---|---|---|---|
| | | 120° | 135° | | | 120° | 135° |
| 1 | 90 | – | 22.0 | 6 | 50 | 5.97 | 8.32 |
| 2 | 80 | 11.2 | 18.0 | 7 | 45 | 5.50 | 6.80 |
| 3 | 70 | 8.50 | 13.0 | 8 | 40 | 5.00 | 6.2 |
| 4 | 60 | 6.85 | 10.7 | 9 | 30 | 4.10 | 4.6 |
| 5 | 55 | 5.95 | 9.40 | 10 | 20 | 2.45 | 3.0 |

inflection at 50 mol. % of urea. Such an S-shaped conductance curve is common for systems in which chemical action occurs [3,4]. The 135° conductance isotherm is steady, not giving any direct indication of the presence of chemical action within the system.

The curves of "derived" conductance (Table 5 and Fig. 5) are similar, the 120° isotherm exhibiting a point of inflection and the 135° curve being monotonous and slightly concave upward.

TABLE 5

| No. | Mol. % $CO(NH_2)_2$ | $\chi \eta \cdot 10^7$ | |
|---|---|---|---|
| | | 120° | 135° |
| 1 | 90 | – | 64.0 |
| 2 | 80 | 43.6 | 55.0 |
| 3 | 70 | 39.6 | 47.0 |
| 4 | 60 | 36.2 | 40.6 |
| 5 | 55 | 34.1 | 36.6 |
| 6 | 50 | 37.5 | 33.1 |
| 7 | 45 | 33.0 | 27.5 |
| 8 | 40 | 30.0 | 25.5 |
| 9 | 30 | 24.4 | 18.8 |
| 10 | 20 | 14.2 | 12.1 |

TABLE 6

| No. | Mol. % $CO(NH_2)_2$ | $\alpha_\chi \cdot 10^6$ |
|---|---|---|
| 1 | 80 | 30.9 |
| 2 | 70 | 28.0 |
| 3 | 60 | 29.3 |
| 4 | 55 | 30.0 |
| 5 | 50 | 22.0 |
| 6 | 45 | 14.2 |
| 7 | 40 | 14.3 |
| 8 | 30 | 7.70 |
| 9 | 20 | 13.4 |

We see that the coordination compound that disturbs the smooth course of the 120° isotherm disappears in the temperature interval from 120 to 135°.

The relative temperature coefficient of conductance is tabulated in Table 6, its curve as a function of composition being plotted in Fig. 6. The curve is quite complex, having a minimum as well as a maximum. The maximum is located

at 55 mol. % of urea. We are not inclined to consider all the singular points on the curve of the temperature coefficient of conductance as indications of the formation of a chemical compound, unless these indications coincide with the results secured by other methods [5].
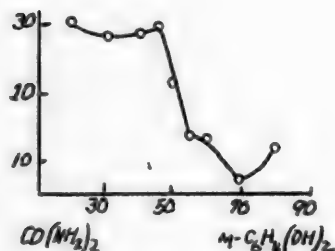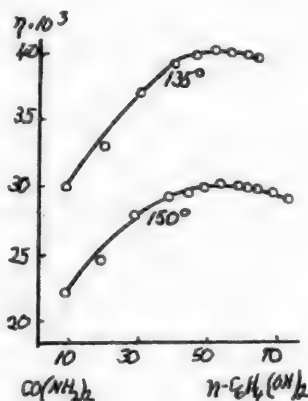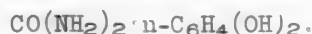


Fig. 6



Fig. 7.

## The Urea — Hydroquinone System

An investigation of this system by the fusibility method disclosed the existence of a considerably dissociated chemical compound:

$$CO(NH_2)_2 \cdot n\text{-}C_6H_4(OH)_2.$$

In our research we used a hydroquinone with a m.p. of 171°.

### Viscosity

The system's viscosity was measured at 135 and 150°, the measurements being listed in Table 7, and the curves of viscosity as a function of concentration being plotted in Fig. 7.

TABLE 7

| No. | Mol. % $CO(NH_2)_2$ | Viscosity $\eta \cdot 10^3$ | | No. | Mol. % $CO(NH_2)_2$ | Viscosity $\eta \cdot 10^3$ | |
|---|---|---|---|---|---|---|---|
| | | 135° | 150° | | | 135° | 150° |
| 1 | 90 | 30.2 | 22.1 | 7 | 45 | 41 | 30.5 |
| 2 | 80 | 33.2 | 24.5 | 8 | 40 | 40.6 | 30.4 |
| 3 | 70 | 37.5 | 27.9 | 9 | 37.5 | 40.4 | 30.3 |
| 4 | 60 | 39.8 | 29.4 | 10 | 35 | - | 30.2 |
| 5 | 55 | 40.4 | 29.6 | 11 | 30 | - | 30.2 |
| 6 | 50 | 41.4 | 30.2 | 12 | 25 | - | 29.6 |

The viscosity isotherms are curves that are concave downward, a maximum being located at 50 mol. % of urea at the lower temperatures. According to the generally accepted interpretation of viscosity isotherms [6], curves of this shape are evidence of chemical interaction within the system, with the maximum giving the approximate composition of the compound produced.

The temperature coefficient of viscosity was calculated (Table 8). The curve showing how it varies with composition (Fig. 8) has a maximum at 50 mol. % of urea.
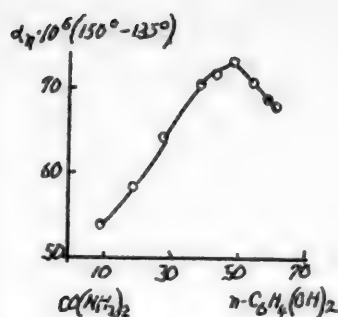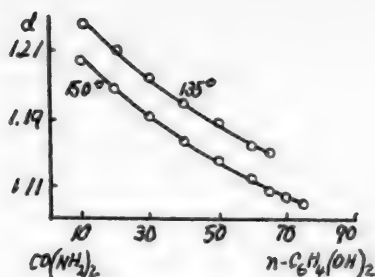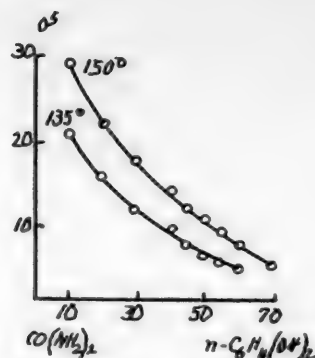
Fig. 8.



Fig. 9.



Fig. 10.

TABLE 8

| No. | Mol. % $CO(NH_2)_2$ | Temperature coefficient of Viscosity $\alpha \cdot 10^6$ (150-135°) |
|-----|------|------|
| 1 | 90 | 54.0 |
| 2 | 80 | 58.0 |
| 3 | 70 | 64.1 |
| 4 | 60 | 69.5 |
| 5 | 55 | 72.1 |
| 6 | 50 | 72.7 |
| 7 | 45 | 70.1 |
| 8 | 40 | 68.1 |
| 9 | 37.5 | 67.5 |

TABLE 9

| No. | Mol. % $CO(NH_2)_2$ | Density 135° | Density 150° |
|-----|------|------|------|
| 1 | 90 | 1.2181 | 1.2072 |
| 2 | 80 | 1.2095 | 1.1990 |
| 3 | 70 | 1.2211 | 1.1901 |
| 4 | 60 | 1.1950 | 1.1840 |
| 5 | 50 | 1.1889 | 1.1780 |
| 6 | 40 | 1.1831 | 1.1723 |
| 7 | 35 | 1.1809 | 1.1699 |
| 8 | 30 | - | 1.1682 |
| 9 | 25 | - | 1.1665 |

The curves of density as a function of the concentration (Table 9 and Fig. 9) at 135 and 150° are slightly concave upward.

## Conductance

The conductance was measured at the same temperatures as the viscosity was, the results being tabulated in Table 10 and the curves of conductance as a function of concentration being plotted in Fig. 10.

The conductance curves, which are slightly concave upward, are smooth, falling from the higher conductance of urea to that of hydroquinone. Curves of this sort, first observed for systems in which there was no chemical interaction [7], were later found to exist in system's exhibiting interaction between their components [4,5].

We then corrected the conductance for viscosity (Table 11 and Fig. 11). This correction made the curves approach straight lines but did not affect their smooth course. Neither the conductance isotherms nor the curves of the "corrected" conductance gave any direct evidence of the existence of chemical interaction within the system.

Table 12 lists the results of our computation of the temperature coefficient

71

TABLE 10

| No. | Mol. % $CO(NH_2)_2$ | Conductance $\underline{x} \cdot 10^5$ | | No. | Mol. % $CO(NH_2)_2$ | Conductance $\underline{x} \cdot 10^5$ | |
|-----|------------|--------|--------|-----|------------|--------|--------|
|     |            | 135°   | 150°   |     |            | 135°   | 150°   |
| 1   | 90         | 20.9   | 29.1   | 6   | 50         | 7.1    | 11.3   |
| 2   | 80         | 16.2   | 22.5   | 7   | 45         | 6.4    | 9.6    |
| 3   | 70         | 12.1   | 18.0   | 8   | 40         | 5.89   | 8.4    |
| 4   | 60         | 9.9    | 14.6   | 9   | 30         | -      | 6.1    |
| 5   | 55         | 8.51   | 12.6   |     |            |        |        |
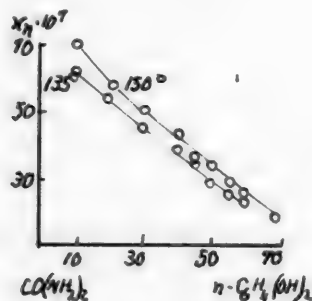


Fig. 11.
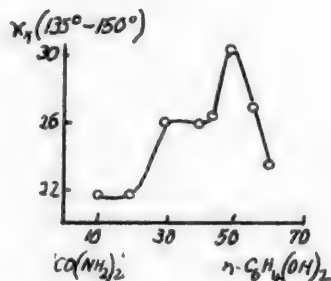


Fig. 12.

of conductance, it being plotted as a function of concentration in Fig. 12.

The shape of the curve is complicated. We find two maxima and two minima, one of the maxima (the higher one) being located at 50 mol. % of urea.

| TABLE 11 | TABLE 12 |
|----------|----------|

| No. | Mol. % $CO(NH_2)_2$ | Conductance times viscosity $\underline{x}\eta \cdot 10^7$ | | No. | Mol. % $CO(NH_2)_2$ | Temperature coefficient of conductance $\alpha_x \cdot 10^6$ |
|-----|------------|--------|--------|-----|------------|------------------|
|     |            | 135°   | 150°   |     |            |                  |
| 1   | 90         | 63.0   | 64.2   | 1   | 90         | 21.8             |
| 2   | 80         | 53.9   | 56.0   | 2   | 80         | 21.7             |
| 3   | 70         | 45.4   | 50.2   | 3   | 70         | 26.2             |
| 4   | 60         | 39.2   | 43.0   | 4   | 60         | 25.7             |
| 5   | 55         | 34.5   | 36.2   | 5   | 55         | 26.0             |
| 6   | 50         | 29.1   | 34.4   | 6   | 50         | 30.5             |
| 7   | 45         | 26.2   | 25.5   | 7   | 45         | 26.7             |
| 8   | 40         | 23.9   | 18.4   | 8   | 40         | 23.5             |
| 9   | 30         |        |        |     |            |                  |

## Evaluation of Results

The viscosity isotherms of the urea — resorcinol system exhibit a maximum at about 45 mol. % of urea, which is shifted toward the more viscous component as the temperature is raised. The conductance isotherm at 120° does not have quite the usual S-shaped course, its point of inflection lying at 50 mol. % of urea. As the temperature is raised, the 135° isotherm assumes the shape of a curve that is

slightly concave upward. Correcting the conductance for viscosity does not affect the shape of the curves. S-shaped conductance curves are known in the literature for systems in which chemical interaction occurs [3,4]. The maximum of the temperature coefficient of viscosity lies at 50 mol. % of urea, while the maximum is displaced from the rational composition to 55 mol. % of urea on the curve of the temperature coefficient of conductance, which is a complicated curve. The course of these curves is evidence of the existence of chemical interaction within the system. The composition of the compound is found to be the same as that established by the fusibility method, namely $CO(NH_2)_2 \cdot m\text{-}C_6H_4(OH)_2$.

In the urea — hydroquinone system the 135° isotherm of viscosity has a maximum at about 50 mol. % of urea. The maximum is obliterated as the temperature is raised. The temperature coefficient of viscosity exhibits a clearly marked maximum at 50 mol. % of urea. The temperature coefficient of conductance is a complicated curve, one of its maxima being located at 50 mol. % of urea. The course of these curves is evidence of the existence of chemical interaction within the system. The composition of the resultant compound $CO(NH_2)_2 \cdot n\text{-}C_6H_4(OH)_2$ is the same as that established by the fusibility method. The smooth conductance isotherms, as well as those of the "corrected" conductance give no indication of the chemical interaction occurring within the system.

## SUMMARY

1. A study has been made of the viscosity, density, and conductance of the following systems: urea — resorcinol at 120 and 135°, and urea — hydroquinone at 135 and 150°.

2. Chemical interaction of the components has been found to exist in the urea — resorcinol system. The compound $CO(NH_2)_2 \ m\text{-}C_6H_4(OH)_2$ is formed.

3. Chemical interaction between the components has been found to exist in the urea — hydroquinone system. The existence of the compound $CO(NH_2)_2 \ n\text{-}C_6H_4(OH)_2$ has been established. This interaction is not shown on the conductance isotherms.

## LITERATURE CITED

[1] D. O. Dionisyev and N. Z. Rudenko, J. Gen. Chem. 22,* 51 (1952).

[2] I. Timmermans, Les solutions concentrees, 522, Paris, VI (1936).

[3] S. Karpachev and V. Stromberg, J. Gen. Chem. 5, 625 (1935).

[4] V. V. Udovenko and R.N. Airapetova, J. Gen. Chem. 17, 425 (1947).

[5] A. S. Naumova, J. Gen. Chem. 19, 1222** (1949); J. Gen. Chem. 19, 1228*** (1949).

[6] N. S. Kurnakov. Introduction to physico-chemical analysis. Moscow-Leningrad (1940).
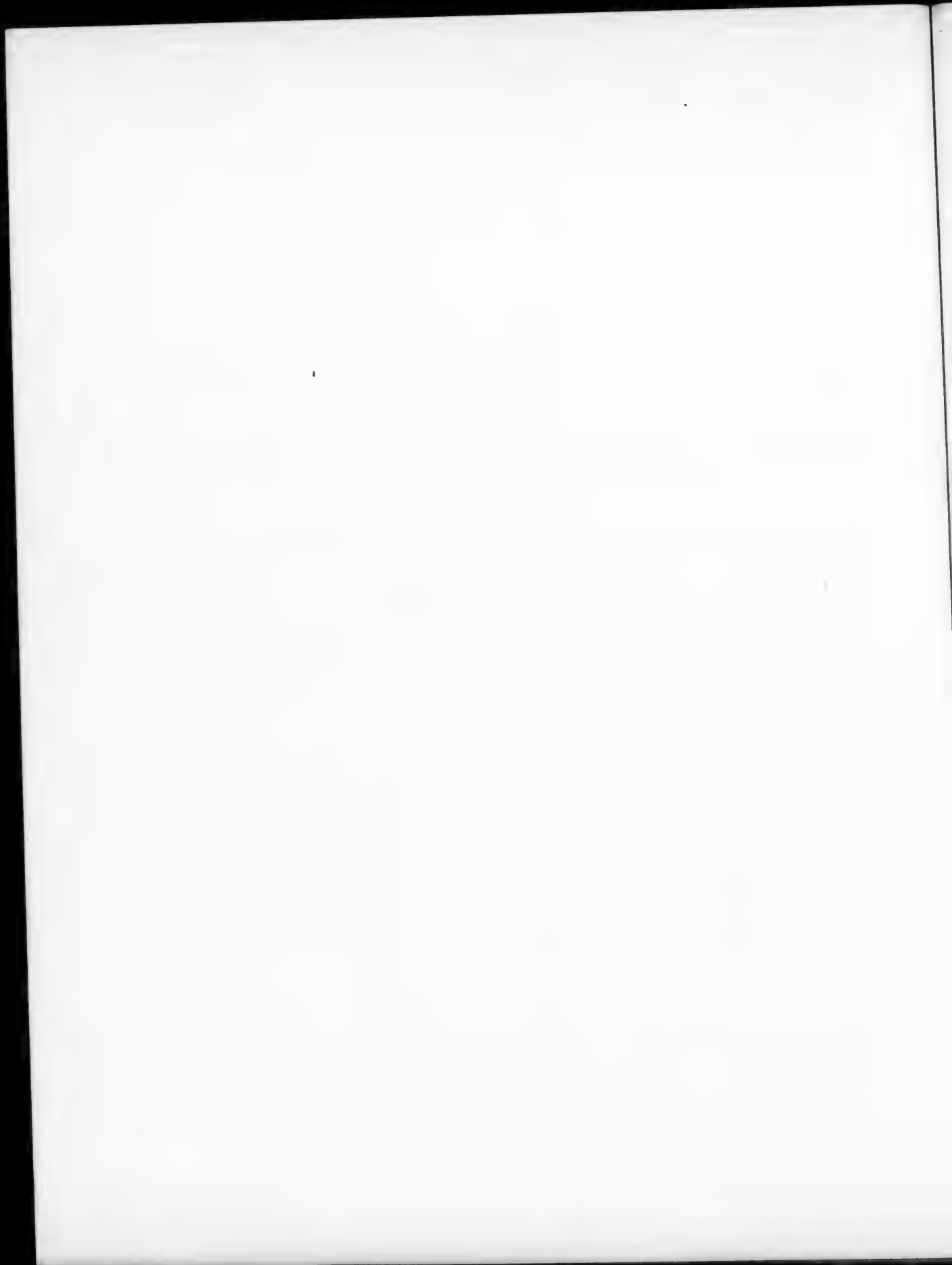
[7] M. I. Usanovich, J. Phys. Chem. 6, 923 (1935).

*See page 59, C.B. English translation.
**See page 1217, C.B. English translation.
***See page 1223, C.B. English translation.

# THE SOLUBILITY OF COPPER, SILVER, AND MERCURY ACETYLIDES

A. K. Babko and M. I. Grebelskaya

The methods of determining acetylene in the control of various production processes chiefly involve the formation of the slightly soluble acetylides of copper, mercury, and silver; however, no research has been done on the solubility of these acetylides, which complicates the choice of a precipitating agent and of appropriate reaction conditions. The scattered data in the literature give rise to doubt whether it is basically possible to employ some of these precipitates. It is stated, for example, that mercurous acetylide is decomposed by potassium cyanide, while, on the other hand, the use of an alkaline solution of mercuric cyanide to effect quantitative precipitation of acetylene is described.

The most important general characteristic of precipitates is their solubility product. Once we know the nature of the equilibrium between the solid phase and the solution, together with the numerical value of the precipitate's solubility product, we can select a reagent and forecast the course of the reaction under various conditions. The solubility product principle has been employed hitherto for the usual precipitates, which are salts of strong electrolytes; moreover, the acetylides of the metals exhibit significant peculiarities. The well-known researches of A. N. Nesmeyanov [1] have shown that in some reactions addition products of the $HgCl_2 \cdot C_2H_2$ type behave like coordination compounds and in others like organometallic compounds. Similarly, $C_2Hg$, mercurous acetylide, where the metal is directly linked to the carbon, behaves like an ordinary salt of the acid $C_2H_2$ in reactions with acids and in other reactions. The properties of acetylene as an acid are involved in another singularity of the acetylides. There are several references in the literature to the absence of any perceptible acidic dissociation of acetylene in aqueous solutions.

Our experiments have shown that the solubility of acetylene in water and in water-alcohol mixtures is not increased (within the margin of experimental error) by the presence of an alkali, i.e., no formation of even a highly hydrolyzed salt of the alkali metal is observed. We know [2] that acetylene displaces ammonia in amides of the alkali metals. Comparing this reaction with the well-known complete decomposition of calcium carbide by water, we may write:

$$2MeNH_2 + C_2H_2 = 2NH_3 + C_2Me_2;$$
$$C_2Me_2 + 2HOH = C_2H_2 + 2MeOH.$$
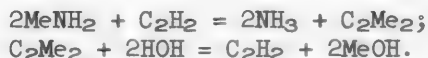
Therefore, the constant of acidic dissociation of $C_2H_2$ must be less than $10^{-14}$ ($K_{H_2O}$), and more than the constant of acidic dissociation of ammonia. The value of the latter is known to be [3]:

$$K_{NH_3} = \frac{[NH_2^-] \cdot [H^+]}{[NH_3]} = 1.9 \cdot 10^{-33}.$$

But determining the dissociation constants directly is impossible for acids whose dissociation is less than that of water. In the light of the peculiarities cited above, a study of the solubility of metal acetylides is of interest in the theory of precipitates, in addition to its practical importance. The present paper reports on an experimental investigation of the solubility of the acetylides of copper, silver, and mercury in acids, the influence of an excess of the precipitating agent, and the reactions of the acetylides with various anions that react with $Cu^+$, $Ag^+$ and $Hg^{++}$. Our results have been processed in accordance with the general theory of precipitates, applying to usual precipitates of the electrolyte type, with allowances made for the singularities of acetylides mentioned above.

The expression for the solubility product has a simple physical meaning for most of the common precipitates, representing the concentration of the ions in direct equilibrium with the precipitate. But a third component, the $H^+$ or $OH^-$ ions, begins to play an extremely important part in the precipitate — solution equilibrium even in some well-known precipitates. We find, for example, from the second dissociation constant of hydrogen sulfide, $K_{H_2S}^{II} = 10^{-15}$ that the $[S^{--}]:[HS^-]$ ratio is $\frac{[S^{--}]}{[HS^-]} = \frac{K_{H_2S}^{II}}{[H^+]} = \frac{10^{-15}}{10^{-14}} = \frac{1}{10}$. even in a highly alkaline solution (at a pH of 14).

Sulfides are therefore hydrolyzed 90% or more even in strongly alkaline solutions. That is why the equilibrium:

$$MeS_{(solid)} \rightleftarrows Me^{++} + S^{--} \tag{1}$$

never applies to sulfides.

Even in strongly alkaline solutions the equilibrium between the solution and the precipitate is governed chiefly by hydrolysis:

$$MeS \text{ (solid)} + HOH \rightleftarrows Me^{++} + HS^- + OH^-. \tag{2}$$

As we know, the equilibrium: $MeS \text{ (solid)} + 2H^+ \rightleftarrows Me^{++} + H_2S$ has been investigated experimentally for metal sulfides.

Once we know the quantities

$$K \text{ equil.} = \frac{[Me^{++}] [H_2S]}{[H^+]^2} \text{ and } K_{H_2S} = \frac{[H^+]^2 [S^{--}]}{[H_2S]} \tag{3}$$

we can calculate the solubility product $L_p = K \text{ equil.} \cdot K_{H_2S}$. The expression giving the $L_p$ for sulfides indicates the energy of the chemical bond between the $Me^{++}$ and $S^{--}$ ions during the formation of the precipitate, but it does not reflect the process itself, which always involves a third component: the $H^+$ ions. This singularity is of even greater importance for the acetylides.

We know that the usual acetylides are completely decomposed by water. The acetylides that are coordination compounds (compounds of $Hg^{++}$, $Ag^+$, and $Cu^+$) are not affected by water, though the equilibrium of a saturated solution must resemble Equation (2):

$$C_2Me_2 \text{ (solid)} + 2HOH \rightleftarrows 2Me^+ + C_2H_2 + 2OH^-. \tag{4}$$

76

The acidic dissociation constant $K_{C_2H_2} = \dfrac{[H^+]^2\,[C_2^{--}]}{[C_2H_2]}$ is unknown for $C_2H_2$ (nor can it be determined directly), so that we cannot calculate $L_p = $
$= [Me^+]^2[C_2^{--}]$.

Thus the only difference between the acetylides and the sulfides is that we know the values of $K_{H_2S}$ for the latter, so that we calculate (but not determine directly) the value of $L_p$; this in turn enables us to place the sulfides on the same footing as ordinary precipitates. Both the metal sulfides and the metal acetylides (plus some other precipitates) must, at bottom, be classed as a special group of precipitates, a saturated solution of which is not characterized by the usual equilibrium with the ions of the precipitate itself, but by the "hydrolytic solubility." The lack of data on the acidic dissociation of acetylene and the special nature of the equilibrium between acetylide precipitates and water cannot, of course, interfere with the quantitative description of all the properties of the sparingly soluble acetylides. Using Equation (4), which corresponds most closely to the actual equilibrium, makes it possible to allow for various singularities of the precipitation and dissolution of the acetylides. It becomes easy, for instance, to explain the seeming contradiction mentioned at the outset of this paper in the data on the course of the reaction in the system consisting of $Hg^{++}$, $CN^{--}$, and acetylene.

The properties of a certain group of precipitates, discussed above, justifies our using the term "hydrolytic solubility product" or "hydrolysis product" to characterize the acetylides; we shall denote this product henceforth by $L_h$. Thus, we get:

$$L_h = [Me^+]^2[C_2H_2][OH^-]^2. \qquad (5)$$

for a $C_2Me_2$ precipitate. This expression indicates that the solubility of acetylides definitely depends upon the concentration of the metal ions, the acetylene concentration, and the pH of the solution.*

## The Solubility of Acetylides in Acids

An experimental check of the solubility of acetylides in acids is of basic importance to corroborate the applicability of the expression for $L_h$. Moreover, increasing the acidity of the solution makes it possible to increase the solubility of acetylides that are only very slightly soluble to values that may be reliably determined by the usual experimental methods. Lastly, it is obvious that data on solubility in acids are of direct interest practically in selecting the conditions of precipitation.

The acetylides were prepared under the conditions ordinarily employed to precipitate them in the determination of acetylene. The acetylene was prepared from calcium carbide and purified by passing it through solutions of iodine and thiosulfate. Cuprous acetylide was precipitated from an ammoniacal solution of copper sulfate with a large excess of hydroxylamine hydrochloride present. Silver acetylide was prepared by precipitation from a coordination compound of silver

---

*If the acidic dissociation constant of acetylene $C_2H_2 \rightleftarrows 2H^+ + C_2^{--}$, should be calculated at some future date by some indirect method or other, it will be easy to calculate the quantity $L_p = [Me^+]^2[C_2^{--}]^2$ from the equation
$$L_p = L_h\,\frac{K_{C_2H_2}}{K^2_{H_2O}}.$$

77

and ammonia, while mercuric acetylide was prepared by passing acetylene through an alkaline solution of mercuric oxide in potassium iodide. The resultant acetylides were washed repeatedly and then placed in bottles and stored under water. Steps were taken to prevent any acetylene from escaping during the determination of solubility.* Measures were also taken to protect the cuprous acetylide against oxidation. This was done by filling the bottles in which the acetylide solubility was determined up to the top with solution, so as to keep all air bubbles out of the bottles. This absence of air inside the bottle made it much harder to stir the liquid, so that the bottle was not attached firmly to the mechanical agitator, but was syspended from it (by rubber tubing). After the solution had been saturated, it was filtered (or it was taken up directly into a pipet through a filtering layer of paper or asbestos); then the liquid was concentrated and its metal content was determined by the usual methods of volumetric analysis.

The results of our experiments on the solubility of silver acetylide are listed in Table 1.

TABLE 1

Solubility of $C_2Ag_2$ in Acids

| No. | Acid | Concentration Of $H^+$ ions used | Concentration of $Ag^+$ ions (found) | $L_h C_2 Ag_2$ $L_h=[C_2H_2][Ag^+]^2[OH^-]^2$ |
|---|---|---|---|---|
| 1 | $HClO_4$ . . . | 1.0 | $2.10 \cdot 10^{-3}$ | $4.5 \cdot 10^{-37}$ |
| 2 | $HClO_4$ . . . | $10^{-1}$ | $0.38 \cdot 10^{-3}$ | $2.7 \cdot 10^{-37}$ |
| 3 | $HNO_3$ . . . | 1.0 | $2.60 \cdot 10^{-3}$ | $8.7 \cdot 10^{-37}$ |
| 4 | $HNO_3$ . . . | $10^{-1}$ | $0.46 \cdot 10^{-3}$ | $4.8 \cdot 10^{-37}$ |
| 5 | $H_2SO_4$ . . . | 1.0 | $1.26 \cdot 10^{-3}$ | $1.0 \cdot 10^{-37}$ |
| 6 | $H_2SO_4$ . . . | $10^{-1}$ | $0.28 \cdot 10^{-3}$ | $1.1 \cdot 10^{-37}$ |
| 7 | $CH_3COOH$ . . | $4.2 \cdot 10^{-3}$ | None found | — |

The last column of the table lists the results of calculations of the hydrolytic solubility product, $L_h$, for $C_2Ag_2$. When the extremely small size of the quantity $L_h$ is borne in mind, the agreement of the results may be regarded as satisfactory. The slightly lower value of solubility in sulfuric acid is due to the fact that in our calculation we assumed that the $H_2SO_4$ is fully dissociated. The variation of solubility with acid concentration (for each of the acids) is characteristic. Changing the acid concentration by a factor of 10 causes a change in solubility by a factor of 5 to 5.4. The equation:

$$C_2Ag_{2(solid)} + 2HOH \rightleftarrows C_2H_2 + 2Ag^+ + 2OH^-, \tag{5a}$$

may be used to calculate the solubility (taking $\underline{x}$ as the concentration of $[Ag^+]$):

---

* The solubility of acetylene in water is not high, totaling only 1.18 gram per liter at 18°, even when its vapor pressure is 1 atmosphere.

$$L_h = x^2 \cdot 0.5x \cdot [OH^-]^2 = 0.5x^3 \cdot [OH^-]^2.$$

It follows that a change of 1000% in the concentration of $OH^-$ (or $H^+$) ions should cause the solubility $\underline{x}$ to change by a factor of $\underline{n} = \sqrt[3]{10^2} = 4.6$, which agrees satisfactorily with the results listed in Table 1.

The results secured for cuprous acetylide (Table 2) exhibit a much less satisfactory agreement.

TABLE 2

Solubility of $C_2Cu_2$ in Acids

| No. | Acid | Concentration of $H^+$ ions used | Concentration of $Cu^+$ ions (found) | $L_h = \dfrac{L_h C_2 Cu_2}{[C_2H_2][Cu^+]^2[OH^-]^2}$ |
|---|---|---|---|---|
| 1 | $HNO_3$ . . . | 1.0 | $1.3 \cdot 10^{-3}$ | $1.2 \cdot 10^{-37}$ |
| 2 | $HNO_3$ . . . | $10^{-1}$ | $1.1 \cdot 10^{-3}$ | $6.7 \cdot 10^{-36}$ |
| 3 | $H_2SO_4$ . . | 1.0 | $1.3 \cdot 10^{-3}$ | $1.2 \cdot 10^{-37}$ |
| 4 | $H_2SO_4$ . . | $10^{-1}$ | $1.0 \cdot 10^{-3}$ | $2.8 \cdot 10^{-36}$ |
| 5 | $CH_3COOH$ . | $4.2 \cdot 10^{-3}$ | $0.50 \cdot 10^{-3}$ | $3.8 \cdot 10^{-34}$ |
| 6 | $CH_3COOH$ . | $1.3 \cdot 10^{-3}$ | $0.34 \cdot 10^{-3}$ | $1.2 \cdot 10^{-33}$ |

We might have supposed that this was due to mechanical contamination of the precipitate or to adsorption of copper at the surface of the $C_2Cu_2$ ions. Experiments to determine solubility, using various quantities of the precipitate yielded nearly identical results, however. A certain lack of agreement among the values for cuprous acetylide is rather due to the fact that the $C_2Cu_2$ precipitate always contains a certain quantity of divalent copper. The presence of $Cu^{++}$ in the precipitate was proved by tests of the solubility of cuprous acetylide in ammonia. These tests yielded values of solubility that approached those for solubility in acetic acid, though the solutions were always colored a perceptible blue. The solubility of cuprous acetylide in acetic acid is lower than in strong acids, but higher than the theoretical value (if we take the expression for $L_h$ as our starting point). In addition to the factors mentioned above, the formation of slightly dissociated copper acetates may also play a part. The solubility of $C_2Cu_2$ in hydrochloric acid is about 30 times as high as in nitric or sulfuric acid. This is doubtless due to the formation of copper chloride complex ions, the solubility of copper acetylide is also raised by the introduction of sodium chloride into the solution. Notwithstanding the discrepancies in our results, the data in Table 2 indicate, in general, that the $L_h$ of $C_2Cu_2$ is higher than that of $C_2Ag_2$. This is fully borne out by the subjoined experiments on the order of solubility of the acetylides. Similar findings that cuprous acetylide has a higher solubility than silver acetylide were secured by Strizhevsky, who calculated $L_{C_2Cu_2}$ and $L_{C_2Ag_2}$ by an indirect method (making no allowance for hydrolysis), based on the concentration ratios of the acetylides and the soluble salts of copper and silver at the instant of equilibrium.

Our investigation of mercuric acetylide disclosed an infinitesimal solu-

bility of the precipitate. In the absence of ions that form coordination com-
pounds, treatment with acids($H_2SO_4$, $HNO_3$, $CH_3COOH$) did not cause any determin-
able quantities of mercury to enter solution. A tiny, though reliably measur-
able, solubility was detected when the precipitate was treated with hydrochloric
acid, which is doubtless due to the formation of coordinated mercury chloride
complex ions: $HgCl_4^{--}$ or $HgCl_3^-$. Calculations based on the assumption that
either of these two complex ions is formed yield a solubility of about this
order of magnitude. We believe it is more likely that $HgCl_3^-$ is formed, since
a complex mercury ion with a coordination number of $4 \cdot (HgI_4^{--})$ is formed, as
we know, only at high iodide concentrations, even in the more stable mercury
iodide complex ions. The dissolution reaction may be represented by the
equation:

$$C_2Hg_{(solid)} + 2H^+ + 3Cl^- = HgCl_3^- + C_2H_2. \tag{6}$$

The mercury in solution was determined iodometrically after it had been
reduced with formaldehyde in an alkaline medium (with KI present); the solu-
bility found experimentally (Table 3, Column 4) corresponds to the overall
mercury concentration, i.e., the concentration of the complex ion $HgCl_3^-$. The
expression:

$$K_{HgCl_3} = \frac{[Hg^{++}][Cl^-]^3}{[HgCl_3^-]} = 10^{-16}.$$

may be used to calculate the concentration of free mercury ions. The value
$10^{-16}$ is taken from Abegg's findings, as well as from our calculations [4].
The concentration of the $[Cl^-]$ ions is known from the experimental conditions,
while that of the $[HgCl_3^-]$ is determined experimentally.

TABLE 3

Solubility of $C_2Hg$ in Acids

| No. | Acid | Concentration of $H^+$ ions used | Solubility (overall mercury concentration) | $L_h = [C_2H_2][Hg^{++}][OH^-]^2 \quad \frac{L_hC_2Hg}{}$ |
|---|---|---|---|---|
| 1 | HCl . . . . | 1.0 | $1.0 \cdot 10^{-3}$ | $1 \cdot 10^{-50}$ |
| 2 | HCl . . . . | $10^{-1}$ | $4.6 \cdot 10^{-5}$ | $2 \cdot 10^{-48}$ |
| 3 | $HNO_3$ . . . | 1.0 | None found | — |
| 4 | $H_2SO_4$ . . . | 1.0 | | — |
| 5 | $CH_3COOH$ . . | $4.2 \cdot 10^{-3}$ | " " | — |

The concentration of $[Hg^{++}]$ ions thus found is substituted in the expres-
sion:

$$L_h = [Hg^{++}][C_2H_2][OH^-]^2. \tag{6a}$$

We know the concentration of OH⁻ ions from the experimental conditions, while (6) indicates that the acetylene concentration equals the overall mercury concentration determined experimentally. $[C_2H_2] = [HgCl_3^-]$. The values of $L_h$ for mercuric acetylide thus calculated are listed in the last column of Table 3.

As we see in Table 3, calculating $L_h$ for mercuric acetylide yields values that are somewhat divergent; in view of the extraordinarily small order of magnitude of this quantity, even minute side reactions affect the computational results considerably.

### The Solubility Series of the Acetylides

The solubility of cuprous, silver, and mercuric acetylides are given above, as well as calculations for the hydrolytic solubility products of these precipitates. These values of $L_h$ enable us to arrange the foregoing acetylides in the following order of solubilities:

$$C_2Cu_2 > C_2Ag_2 > C_2Hg. \tag{7}$$

We were interested in making an experimental check of the applicability of the law of series [5] generally adopted for other precipitates to the acetylides in order to confirm this order of the values of $L_h$.

Cuprous acetylide  The red-brown precipitate of $C_2Cu_2$ turns black when treated with a solution of $AgNO_3$. After having been agitated for 2 hours with an excess of 0.05N $AgNO_3$, the precipitate was filtered out and washed. $Cu^{++}$ was detected in the solution, nothing but silver being found in the precipitate. Thus, the reaction:

$$C_2Cu_{2\,(solid)} + 2Ag^+ = C_2Ag_{2\,(solid)} + 2Cu^+, \tag{8}$$

goes to completion, being governed, not by adsorption, but by the ratio between the $L_h$ of the precipitates, in conformity with the results obtained above. The monovalent copper produced as the result of Reaction (8) was oxidized by the excess $AgNO_3$, yielding metallic silver and $Cu^{++}$  The red-brown precipitate of $C_2Cu_2$ turns white when treated with a 0.05N solution of $HgCl_2$. The exchange is complete in this case, too, nothing but mercury being found in the precipitate (no copper being detected).

Silver acetylide.  The white precipitate of $C_2Ag_2$ did not change color when treated with an ammoniacal solution of monovalent copper. No copper was detected in the precipitate, while no silver was found in the solution. Thus, in conformity with the relative values of $L_h$ derived above, Reaction (8) does not go to the left, even when a large excess of $Cu^+$ is present. Nor is the color of the precipitate changed when the $C_2Ag_2$ is treated with a solution of $Hg(NO_3)_2$, nothing but mercury being found in the precipitate and nothing but silver in the solution. These tests likewise serve as full confirmation of the ratios derived above.

Mercuric acetylide.  No change in color is observed when the white precipitate of $C_2Hg$ is treated with solutions of $Cu^+$ or $Ag^+$ salts, nor is copper or silver detected in the solid phase.

Hence, all the experiments described above confirm that the direction in which the reaction will go during the formation and dissolution of acetylides may be predicted from the general theory of precipitates and in conformity with the values we have found for $L_h$.

81

## Effect of an Excess of the Precipitating Agent

One of the principal corollaries of the solubility product principle, as we know, is that of the effect of like ions upon the solubility of the precipitate. Three components are formed in the hydrolytic dissolution of acetylides: ions of the metal, molecules of $C_2H_2$, and $OH^-$ ions. An increase in the concentration of any of these components ought to diminish the concentration of the other two accordingly. If the general postulates of the theory of precipitates are applicable to the acetylides notwithstanding their chemical singularities, this effect ought to exist. This is of considerable importance in selecting the conditions required for determining acetylene. The effect of an excess of the metal ion or of acetylene can be studied experimentally only in an acidic medium. At high values of pH, the solubility of the acetylides of copper, silver, and mercury is too low (provided there are no other forms of interaction present, such as the formation of new precipitates or of complex ions) to make the quantitative determination of solubility dependable.

We cite below our experiments on the change in the solubility of silver acetylide in 1N sulfuric acid produced by the addition of an excess of $AgNO_3$ or of acetylene to the solution. After the solution had been saturated, it was filtered and concentrated with $HNO_3$, and the silver was determined by titration. In the former case (with an excess of $Ag^+$ present), the increase in the percentage of silver in the solution due to the dissolution of the $C_2Ag_2$ depended upon the acetylene. We see from Equation (5a) that when the solution pH is constant:

$$[Ag^+]^2[C_2H_2] = \text{const}.$$

An excess of silver ions must therefore sharply reduce the solubility of the precipitate, while an excess of acetylene will lower solubility much less. The results of our tests, reproduced in Fig. 1, bear out this conclusion.
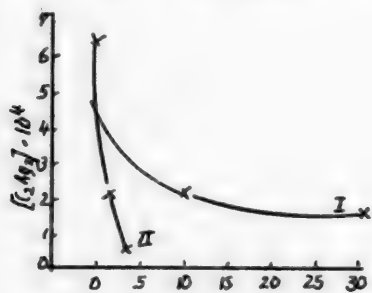


The pH has a profound effect upon the solubility of the acetylides. The variation of solubility with pH in an acid medium has been discussed earlier. At a pH $> 7$ the solubility of acetylides is so small (in accordance with the $L_h$) as not to be measurable directly. Several tests have confirmed that this also holds good, in conformity with the $L_h$, in an alkaline medium. Let us consider, by way of example, the reaction of silver acetylide with potassium iodide.

This reaction may be represented schematically[*] as follows:

Fig. 1. Solubility of silver acetylide in 1N $H_2SO_4$ with an excess of the precipitant present.

I – Excess $[C_2H_2] \cdot 10^3$;

II – Excess $[Ag^+] \cdot 10^3$.

---

[*] A more detailed investigation, on the basis of which we have evolved an acidimetric method for determining acetylene, shows that a soluble iodide complex ion of the $AgI_2^-$ type is formed when $C_2Ag_2$ is treated with a concentrated solution of KI.

$$C_2Ag_2{}_{(solid)} + 2I^- + 2H_2O \rightleftharpoons 2AgI_{(solid)} + C_2H_2 + 2OH^-. \tag{9}$$

The constant of this equilibrium is:

$$K_{equil.(9)} = \frac{[C_2H_2][OH^-]^2}{[I^-]^2} = \frac{L_h}{L_{AgI}^2} = \frac{4 \cdot 10^{-37}}{(10^{-16})^2} = 4 \cdot 10^{-5}. \tag{10}$$

If we treat silver acetylide with a 1N solution of potassium iodide, evidently $[I^-] = 1$ and $[OH^-] = 2[C_2H_2]$. Bearing in mind (10), we get:

$$4[C_2H_2]^3 = 4 \cdot 10^{-25}, \tag{11}$$

whence:

$$[C_2H_2] = 2.2 \cdot 10^{-2} \tag{11a}$$

(if the formation of the complex ion $AgI_2^-$ is borne in mind, we get an even higher value). This value approaches the solubility of acetylene in water, so that we may expect the 1N solution of KI to decompose silver acetylide, yielding acetylene. This has been fully confirmed by experiment – when $C_2Ag_2$ is treated with a 1N solution of KI, acetylene is evolved vigorously and an equivalent quantity of alkali is formed. When silver acetylide is treated with 1N KI in the presence of an excess of alkali, say, at $[OH^-] = 1$, we get, in conformity with (10):

$$[C_2H_2] = K_{equil.} \frac{[I^-]^2}{[OH^-]^2} = K_{equil.} = 4 \cdot 10^{-5}. \tag{12}$$

Comparison of this value with (11a) shows that in the presence of an alkali the concentration of the acetylene evolved is much less than its solubility in water. As a matter of fact, silver acetylide is decomposed only very slightly indeed by potassium iodide when a 1N alkali is present. The ratio between the reacting components in the solution containing $Hg^{++}$ and $CN^-$ ions and acetylene is explained in a similar fashion. The equilibrium looks like this:

$$C_2Hg_{(solid)} + 4CN^- + 2H_2O \rightleftharpoons Hg(CN)_4{}^{--} + C_2H_2 + 2OH^-. \tag{13}$$
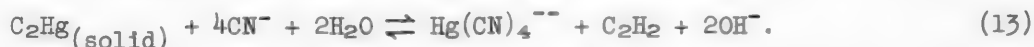
Taking the mean of the values of $L_h = 10^{-49}$ derived above for the solubility of $C_2Hg$, and the quantity:

$$K_{Hg(CN)_4{}^{--}} = \frac{[Hg^{++}][CN^-]^4}{[Hg(CN)_4{}^{--}]} = 10^{-42},$$

for the mercuric cyanide complex ion [6], we get:

$$K_{equil.(13)} = \frac{[Hg(CN)_4{}^{--}][C_2H_2][OH^-]^2}{[CN^-]^4} = \frac{L_h}{K_{Hg(CN)_4{}^{--}}} = \frac{10^{-49}}{10^{-42}} = 10^{-7}. \tag{14}$$

When mercuric acetylide is treated with a 1N solution of potassium cyanide, the concentration of the reaction products: $Hg(CN)_4{}^{--}$, $C_2H_2$, and the $OH^-$ ions, will then be $\underline{x}$, $\underline{x}$, and $2\underline{x}$. In conformity with Equation (14), we get $4x^4 = 10^{-7}$, whence $\underline{x} = [C_2H_2] = 1.3 \cdot 10^{-2}$, i.e., a value approaching the solubility of acetylene in water. As a matter of fact, the mercuric acetylide is decomposed by potassium cyanide, giving off acetylene. At first glance, this fact forces us to consider

one of the methods used for determining acetylene, based on precipitating it from an alkaline solution of mercuric cyanide, as completely unreliable. Further consideration of Equilibrium (13), however, leads us to another conclusion. For instance, let acetylene in a concentration (initial $C_2H_2$) of $0.25 \cdot 10^{-2}$ be added to a 0.1N solution of $K_2Hg(CN)_4$ in 1N KOH; then Reaction (13) will be shifted to the left to a large extent, and we get a concentration of $[CN^-]$ ions = 4 (initial $C_2H_2$) = $10^{-2}$ in the solution.[*] From Equation (14) we get:

$$[C_2H_2] = \frac{K_{equil.}[CN^-]^4}{[OH^-]^2[Hg(CN)_4^{--}]} = \frac{10^{-7} \cdot 10^{-8}}{10^{-1}} = 10^{-14},$$

i.e., the concentration of unreacted acetylene remaining in equilibrium with the alkaline solution of $K_2Hg(CN)_4$ will be negligible. Therefore, although $C_2Hg$ is decomposed by potassium cyanide, an alkaline solution of mercuric cyanide is quite serviceable for the quantitative determination of acetylene, owing to the high concentration of hydroxyl ions.

### The Reactions of Silver, Copper, and Mercury
### Acetylides With Various Reagents

We were interested in the behavior of the acetylides with various reagents that form precipitates or coordination compounds with $Ag^+$, $Cu^+$, and $Hg^{++}$, in order to learn the conditions governing the formation and decomposition of these acetylides. The following reagents were tested: $Na_2S$, KCN, KI, KBr, KCNS, $K_4Fe(CN)_6$, $Na_2S_2O_3$, and NaCl. Wherever possible we computed the equilibrium concentration of the acetylene evolved when the respective acetylide was treated with each of these reagents. This calculation was performed by a method resembling that discussed above for the acetylides of mercury and silver. Wherever the dissociation constant of the respective complex ion, such as $AgI_2^-$, was known, we assumed that these complex ions were formed in the concentrated solutions of the respective reagents (a detailed discussion of these calculations would require too much space). A high concentration of acetylene secured in these calculations was evidence of the instability of the given acetylide under the stated conditions. The results of an experimental check, listed in the respective columns of Table 4, are in satisfactory agreement with the bulk of our calculations.

---

[*]Should Equation (13) shift to the left to a small extent, the concentration of $[CN^-]$ ions would be even lower, which might facilitate the leftward course of the reaction still more.

---

# TABLE 4

## Reaction of the Acetylides of Silver, Copper, and Mercury with Various Anions

| No. | Reagent | Reagent concentration mol per liter | Cuprous acetylide Evolution of $C_2H_2$ | | Silver acetylide Evolution of $C_2H_2$ | | Mercuric acetylyde Evolution of $C_2H_2$ | |
|---|---|---|---|---|---|---|---|---|
| | | | Theoret. Mol./l. | Exper. | Theoret. Mol./l. | Exper. | Theoret. Mol./l. | Exper. |
| 1 | $Na_2S$ | 0.1 | $6.0 \cdot 10^{+2}$ | $*$ | $8.7 \cdot 10^{+15}$ | $*$ | $3 \cdot 10^{+4}$ | $*$ |
| 2 | KCN | 0.1 | $9.4 \cdot 10^{+4}$ | | $1.9 \cdot 10^{+4}$ / $1.4 \cdot 10^{-2}$ | | $1.3 \cdot 10^{-3}$ | |
| 3 | KI | 1.0 | $8.2 \cdot 10^{-5}$ | No $C_2H_2$ found | $1.1 \cdot 10^{-4}$ | Slight decomposition | $1.5 \cdot 10^{-5}$ | |
| 4 | KBr | 1.0 | $5.5 \cdot 10^{-6}$ | | $5.4 \cdot 10^{-6}$ | | $1.0 \cdot 10^{-7}$ | |
| 5 | NaCl | 1.0 | $4.9 \cdot 10^{-6}$ | | $4.5 \cdot 10^{-5}$ | | $4.5 \cdot 10^{-9}$ | |
| 6 | KCNS | 1.0 | $2.6 \cdot 10^{-4}$ | | $6.7 \cdot 10^{-3}$ | | $1.3 \cdot 10^{-7}$ | |
| 7 | $Na_2S_2O_3$ | 1.0 | — | $C_2H_2$ evolved | $1.0 \cdot 10^{-6}$ | No $C_2H_2$ found | — | No $C_2H_2$ found |
| 8 | $K_4Fe(CN)_6$ | 0.1 | — | No $C_2H_2$ found | — | — | — | |

$*$ $CuCu_2$ completely decomposed.

## SUMMARY

It has been shown that the equilibrium of saturated solutions of the acetylides of mercury, silver, and copper is described by a hydrolytic solubility:

$$C_2Me_{2(solid)} + 2H_2O = 2Me^+ + C_2H_2 + 2OH^-.$$

This relationship may be expressed by the "hydrolytic solubility product":

$$L_h = [Me^+]^2[C_2H_2][OH^-]^2.$$

An experimental study has been made of the solubility of the acetylides of $Hg^{++}$, $Ag^+$, and $Cu^+$ in acids, and $L_h$ has been calculated for $C_2Ag_2$ ($4 \cdot 10^{-37}$), for $C_2Cu_2$ ($3 \cdot 10^{-36}$), and for $C_2Hg$ ($10^{-49}$).

The applicability of the series rule to the acetylides of copper, silver, and mercury has been tested. The effect of an excess of the equilibrium components: $Me^{+n}$, $C_2H_2$, $OH^-$, upon the hydrolytic solubility has been investigated experimentally, the results being in satisfactory agreement with the reagents.

A study has been made of the reaction of these acetylides with various anions that combine with the cation of the precipitate; it has been shown that the calculated stability of the acetylides is satisfactorily confirmed by experiment.

These results make it possible to apply the general theory of precipitates to the calculation and prediction of the practical conditions required for the precipitation and dissolution of acetylides, bearing in mind certain specific features of precipitates of this type.

## LITERATURE CITED

[1]  A. N. Nesmeyanov, R. Kh.  Freidlina, and Ya. E. Borisov, <u>Jubilee Symposium of the USSR Acad. Sci. on the 30th Anniversary of the Great Socialist October Revolution I</u>,  656 (1947).

[2]  J. Nieuwland and R. Vogt.  <u>The chemistry of acetylene</u> (Russ. ed.), 75.  State Publishing House for Foreign Literature (1947).

[3]  A. I. Shatenshtein.  <u>Theory of acids and bases</u>, 265.  State Chemical Press (1949).

[4]  A. K. Babko, <u>Jubilee Symposium of the USSR Acad. Sci. II</u>, 138 (1942).

[5]  N. A. Tananayev, <u>Chem. Prog</u>. 10, 5, 621 (1941).

[6]  W. Latimer, <u>The Oxydation States of the Elements</u>, p. 166 (1938).

# A CALORIMETER FOR MEASURING THE LATENT HEAT OF VAPORIZATION
## OF HIGHLY VOLATILE LIQUIDS AT VARIOUS TEMPERATURES

S. M. Skuratov and O. N. Kachinskaya

The indirect methods of determining the latent heat of vaporization of liquids sometimes fail, so that a direct experimental determination is always preferable. In our literature, however, not enough work has been done on the procedures involved in direct determinations. The procedure we propose makes it possible to measure the latent heat of vaporization of highly volatile liquids at temperatures that range from room temperature to 100°, using only very small quantities of the substance (a few grams) and securing results with an accuracy of 1% though employing comparatively simple apparatus.

Method. Some 1 to 2 grams of the substance under test is placed in a glass ampoule of special design. The ampoule is then placed in a depression in a massive copper cylinder, which serves as the calorimeter. Evaporation is effected by passing air, previously heated to the temperature of the calorimeter, through the layer of liquid in the ampoule, the amount of liquid vaporized being determined by the weight of the ampoule before and after the test, which is run under adiabatic conditions. The change in the calorimeter's temperature during the run enables us to calculate the substance's heat of vaporization, provided we know the heat capacity of the calorimeter system. The latter is determined in special experiments, involving the supply of heat by an electric current. The principle on which the calorimeter employed in the present research is based is the same as that of the calorimeter previously described by one of the present authors [1] for determining the true heat capacity of solids and liquids. The same principle is employed in the calorimeter suggested by Swietoslawski [2] for measuring the heats of adsorption and vaporization of highly volatile substances. But in the Swietoslawski calorimeter vaporization takes place without the passage of a current of air through the substance. This greatly increases the length of the run (ranging from 3 to 8 hours, depending upon the volatile liquid involved), thus requiring extraordinarily close control of the calorimeter's heat losses if reliable results are to be secured. In the procedure

we suggest vaporization is speeded up by the passage of an air current, as stated above. Smith [3] was the first one to employ the blowing of air through the substance, and the blowing through of air has been used with great success in the well-known original method due to Vrevsky [4]. The theory of this method is set forth in detail in the papers by Goff and Hunter [5] and by Hunter and Bliss [6], who indicate what corrections have to be applied to the observed readings to allow for the interaction of the vapor molecules with the molecules of the air blown through. The total of these corrections do not exceed 0.1% of the observed values, however, and may be ignored in our case. It should be pointed out that in all the papers cited, where gas is passed through in order to speed up vaporization, large calorimeters are employed, which require large quantities of the substance under test. The details of our procedure are set forth below.

### Calorimeter.

The calorimeter (Fig. 1) was a massive copper cylinder (a), 45 mm in diameter and 75 mm high with a slightly conical hole bored into it to hold the ampoule containing the test substance. The calorimeter was suspended by 3 strings inside a thin-walled brass shell (b), the cover of which was secured by 8 screws, a rubber gasket being used to ensure airtightness. The clearance between the wall of the calorimeter and the shell was 15 mm.
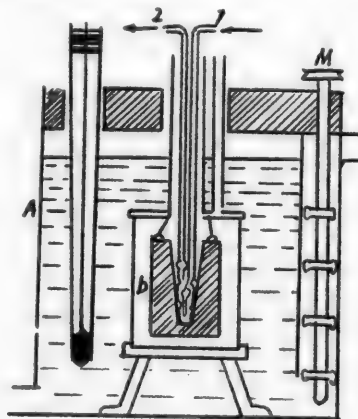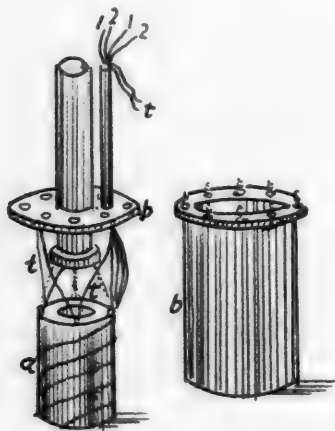


Fig. 1. Calorimeter and shell.     Fig. 2. Cross-sectional view of the calorimeter and its water jacket.

The shell and the calorimeter were placed on a special stand inside an outer jacket (A) (Fig.2) with a capacity of some 10 liters, which was filled with water. The water in this jacket was thoroughly stirred by a propeller stirrer (M), rotating at 1500 rpm. By adding hot water (from a boiler) or cold (from a water tap) to the jacket via special stopcocks, we were able to set up the desired temperature within the jacket and to maintain it to within 0.001-0.002°. In the tests run at 40° and 60° the jacket's heat losses were so high that we found it desirable to supplement the addition of hot water by supplying heat to the jacket via a heating coil of nichrome wire immersed in the water. The coil was arranged within the jacket in such a way as to ensure an even distribution of the heat throughout the jacket. The current passing through this coil was regulated so that the heat evolved compensated for nearly all the heat lost by the jacket to

the space surrounding it. Close regulation of the jacket temperature was achieved by adding hot or cold water in small quantities.

The temperature difference between the calorimeter and its water jacket was measured by the emf of a thermopile, consisting of 3 copper-constantan thermocouples (t), one junction of each of which was secured by Bakelite to the outer wall of the calorimeter, with the other junctions attached to the cover of the brass shell (Fig. 1). The emf of the thermopile was read off on a mirror galvanometer, whose voltage sensitivity was such that a calorimeter-shell temperature difference of 0.0003° could be read. This calorimeter design enabled us to gauge changes in its temperature from changes in the temperature of the jacket, without having to read the calorimeter's temperature. A preliminary test was made of the thermopile, so that we had complete certainty of there being no stray sources of emf in its circuit. The jacket temperature was measured with a Beckmann thermometer. Reading the thermometer in degrees, as well as any other correction to its reading, was rendered unnecessary by the fact that the heat capacity of the calorimeter system was measured in every case by the amount of heat supplied electrically, these tests being run, whenever possible at the same range of the thermometer's scale as that employed in the determination of the heat of vaporization.

To determine its heat capacity the calorimeter was equipped with a heating coil (c) (Fig. 1) — a manganin wire with a resistance of 10.5 ohms, affixed by means of Bakelite to (and electrically isolated from) the outer surface of the calorimeter. Each end of the heating coil was led outside through two copper leads (passing through a tube soldered to the cover of the shell). One pair of leads (1,1) served as a heating current supply, while the other (2,2) was used to measure the voltage across the end of the heating coil.

Ampoule for vaporizing the substance. The design of the glass ampoule is seen in Fig. 3. Its dimensions were such as to fit tightly within the hole bored into the calorimeter. Still greater tightness was secured by covering the side walls of the ampoule with several thicknesses of aluminum foil; this ensured good heat transfer between the ampoule and the calorimeter. Two glass tubes, attached by means of ground-glass joints, served the following purposes: one passed air into the ampoule through the layer of the substance (1), while the other (2) carried off the vapor to an absorber. Tube 2 was equipped with a bulb (3) to prevent any liquid condensing from the exhaust vapor from flowing back to the ampoule. When the ampoule was weighed before and after the run, the tubes were disconnected and replaced by ground-glass stoppers (4). A plug of glass wool was placed in the expanded section (5) to retain any liquid spray that might be carried along by the passage of air. The air passing through the layer of liquid in the ampoule must be first freed of dust, dried, and heated to the temperature of the calorimeter Moreover, provision must be made for the fine adjustment of the rate of air flow, which must be held constant.

The design of the drying system is visible in Fig. 4, where 1 and 1 are large-capacity vessels to create pressure (since only little air was consumed in each test, the pressure could be regarded as constant), 2 is a vessel for observing the rate of air flow, 3 and 9 are micrometric regulating valves, and 4-8 are the absorbing bottles.

Before entering the calorimeter, the air passed through the drying system and then through a coil consisting of a thin-walled copper tube, 2 mm in diameter and 4 meters long. This coil was immersed in the water of the calorimeter jacket. Preliminary tests showed that tubing of this length made sure that the

air was warmed up completely at the flow rates employed. The air thus dried and warmed was passed through the layer of liquid under test in the ampoule placed within the calorimeter. The vapor of the substance was carried off through the tube 2 and condensed in a condenser or collected in appropriate receivers, depending upon the nature of the liquid.

Running the experiment. The test was run as follows. The ampoule containing the substance under test was first weighed to the nearest 0.1 mg and then packed tightly into the calorimeter. To prevent the liquid from evaporating during the preliminary test period, rubber tubing fitted over the ends of the ampoule tubes was closed off by clamps. The calorimeter (a) (Fig.1) was placed within the shell (b), the latter's cover was screwed down tight (gasket), and the shell was placed in the water jacket (A) (Fig. 2). The calorimeter suspension was so designed as to make it possible to lower the calorimeter to the bottom of the brass shell in order to speed up the attaining of thermal equilibrium between the calorimeter and the shell. As soon as equilibrium was established, the calorimeter was raised again, and the calorimetry test, consisting of initial, principal, and terminal periods as a rule, was run. The initial test period was run solely to determine the initial temperature of the calorimeter accurately. In the principal period, air that had been previously dried and warmed as described above was passed through the layer of substance in the ampoule, causing the temperature of the calorimeter to drop as a result of evaporation. To keep the test conditions adiabatic the temperature of the water jacket was lowered to the same extent (by adding cold water). We were able to run the test under such conditions that the required correction for incompletely adiabatic conditions was always less than 0.001° and could be ignored.

The substance was evaporated very slowly as a rule (0.4 − 0.5 g of the substance being evaporated within about 1 hour at 20°). The temperature of the calorimeter dropped by only 0.3 − 0.4° during the entire run. This eliminated any possibility of supercooling the liquid below the calorimeter's temperature, so that the process could be regarded as isothermal. The terminal period of the test involved the finding of the equilibrium temperature of the calorimeter after the run was over.

Determining the heat capacity of the calorimeter system. The heat capacity of the calorimeter system (including the ampoule and the test substance) was determined in special tests by electric heating. The same calorimetric test was made, the sole difference being that a previously fixed value of electric current was passed through the calorimeter heating coil during the principal test period instead of vaporizing the substance. Adiabatic conditions were ensured by adding hot water to the jacket. The amount of electric energy passing through the calorimeter heating coil was measured by means of the usual compensation circuit. The time during which the current flowed was measured by a stop watch. The stop watch and the instruments used to measure the electric energy were first checked to make sure that the overall absolute error in reading the electric energy could not exceed 0.05%. The relative accuracy of the tests could not exceed 0.5% owing to the extremely small temperature rise during the runs (0.3 − 0.4°).

Table 1 gives an example of the determination of the heat capacity of the calorimeter system at 40°.

TABLE 1

Heat Capacity of the Calorimeter System at 40°

| Test No. | I | E | $\tau$ | Q | $\Delta\vartheta$ | W | Mean value of $\underline{W}$ |
|---|---|---|---|---|---|---|---|
| 20 | 0.14468 | 0.7060 | 311.7 | 20.33 | 0.282 | 72.1 | |
| 21 | 0.14051 | 1.6590 | 565.3 | 31.48 | 0.437 | 72.0 | |
| 23 | 0.14134 | 1.6692 | 419.3 | 23.63 | 0.331 | 71.4 | |
| | | | | | | | 71.7±0.5% |
| 25 | 0.14100 | 1.6658 | 513.8 | 28.83 | 0.402 | 71.7 | |
| 35 | 0.21293 | 2.5161 | 245.6 | 31.43 | 0.442 | 71.1 | |

<u>Notation</u>: I — heating coil current, amperes; $\underline{E}$ — voltage across the heating coil, volts; $\tau$ — time in seconds; $\underline{Q}$ — amount of heat evolved by the current, calories; $\Delta\vartheta$ — rise of calorimeter temperature, standard degrees; $\underline{W}$ — heat capacity of the calorimeter system.
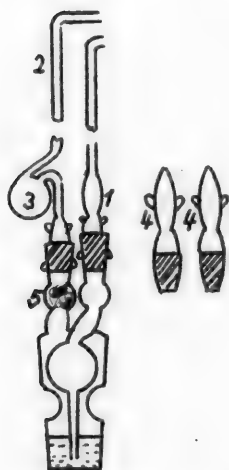


Fig. 3. Ampoule for vaporizing the substance.
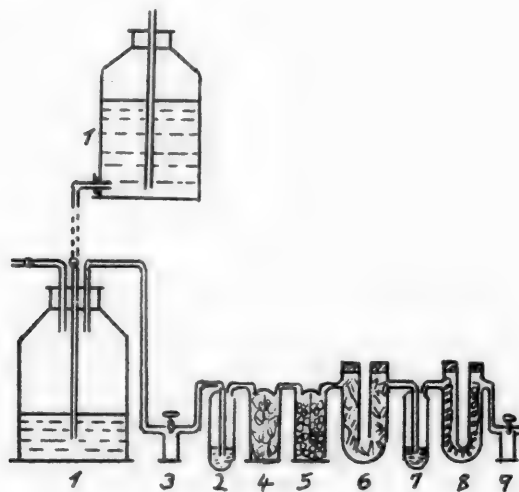


Fig. 4. Drying system.

<u>Testing the procedure</u>. Before investigating the heat of vaporization of the object under test, we felt it was necessary to check the procedure by determining the heat of vaporization of some substance that had been investigated already. We could not use water for this purpose, since its high heat of vaporization and low volatility would necessitate another type of calorimeter. The

only organic liquid of adequate purity at our disposal was toluene. We therefore had to employ it in this procedural check, notwithstanding·the fact that the data in the literature on the heat of vaporization of toluene are extremely scanty. The results we secured for the heat of vaporization of toluene at 40° are given below (Table 2).

TABLE 2

| Test No. | Grams of substance vaporized | Change in calorimeter temperature, standard degrees | Calorimeter heat capacity, calories/ standard degree | Heat of vaporization, calories/gram |
|---|---|---|---|---|
| 1 | 0.3690 | 0.502 | 71.7 | 97.5 |
| 2 | 0.3412 | 0.459 | 71.7 | 96.4 |
| 3 | 0.2877 | 0.391 | 71.7 | 97.4 |
| | | | Average .......... | $97.1 \pm 0.5\%$ |

Kolosovsky and Alimov [7] found the latent heat of vaporization of toluene to be 98.5 calories per gram at 42.85°. This value differs by only 1.4% from the value found by us. This agreement is highly satisfactory, when we bear in mind that there often is a difference of 3-5% between the figures given by various authors for the heats of vaporization of organic substances. It is unlikely that descrepancies of this order are due to methodological errors; it is more likely that they are caused by the insufficient purity of the substances tested. The agreement of the values cited above justifies our inferring that there are no significant systematic errors in our procedure.

We wish to express our thanks to Prof. M. M. Popov for his counsel during the planning and performing of this research.

LITERATURE CITED

[1]  S. M. Skuratov, Colloid Jour. 1947, 9, 133.

[2]  W. W. Swietoslawski. Microcalorimetry, 127. New York (1946).

[3]  A. W. Smith, Phys. Review, 25, 145 (1907); 33, 173 (1911).

[4]  M. S. Vrevsky, Jour. Russ. Phys. Chem. Soc. 59, 69, 77 (1927).

[5]  J. A. Goff and J. B. Hunter, J. Appl. Mech., 9, 21 (1942).

[6]  J. B. Hunter and H. Bliss, Ind. Eng. Chem., 36, 945 (1944).

[7]  N. Kolosovsky and A. Alimov, Bull. Soc. Chim., I, 877 (1934).

The Prof. V. F. Luginin Thermal Laboratory, Moscow State University.

# SULFANURYL CHLORIDE

## A. V. Kirsanov

The acid with the structure of N≡SOOH, which is unknown at the present time, ought to possess physical and chemical properties that reflect its own peculiar singularities, though it ought to resemble cyanic acid in some respects. That is why the acid with the structure of N≡SOOH should be called sulfanic acid, by analogy with cyanic acid. It is very likely that sulfanic acid or its tautomer sulfimide are intermediate products in the amidation of carboxylic acids and in the synthesis of imidosulfamide [1].

Not a single derivative of sulfanic acid is known at the present time. It is the objective of the present research to secure either sulfanic acid or one of its derivatives and to investigate their properties.

Sulfimide, which is tautomeric with sulfanic acid and for which a better name would be isosulfanic acid, is likewise unknown, though some of its derivatives are known. Traube [2] assumed that he had secured the silver salt of sulfimide from the reaction products of sulfuryl chloride and ammonia, as well as from the products of the thermal decomposition of sulfamide. Traube secured other salts of "sulfimide" by double decomposition reactions with this silver salt. Hantzsch [3] has shown that Traube's salts were salts of a trimer of sulfimide, the so-called trisulfimide, which it would be better to call isosulfanuric acid, by analogy with isocyanuric acid. Hantzsch's efforts to secure free isosulfanuric acid met with failure. Decomposition of the silver salt was always accompanied by acidolysis, producing a small yield of imidosulfamide [3]. Reacting the silver salt of isosulfanuric acid with methyl iodide and benzoyl chloride, Hantzsch secured the respective trimethyl and tribenzoyl derivatives. Hantzsch also describes a sulfomelide analogous to cyamelide, but we can hardly consider his data on sulfomelide reliable, inasmuch as he was unable to secure sulfomelide in the crystalline state and his description of the experiments involved in the synthesis of sulfomelide is not notable for its clarity. Thus, only a few derivatives of isosulfanuric acid, difficult of access, are known at the present time, while not a single derivative of sulfanuric acid is known.

There were two possible ways of synthesizing derivatives of sulfanic acid: the thermal cleavage of sulfamide and its metallic derivatives in the expectation of securing the respective salts of sulfanic acid, as follows:

$$NH_2SO_2NH_2 \rightarrow N\equiv SOONH_4$$

$$NH_2SO_2NHNa \rightarrow N\equiv SOONa+NH_3,$$

and the thermal cleavage of trichlorophosphazosulfuryl chloride [4] in the expectation of securing sulfanyl chloride (the acid chloride of sulfanic acid) or its polymers (such as sulfanuryl chloride), as follows:

$$ClSO_2N=PCl_3 \rightarrow POCl_3+N\equiv SOCl \rightarrow (N\equiv SOCl)x.$$

The latter reaction is similar to the thermal cleavage of esters as well as to the thermal cleavage of acylsulfamic acids [5]. It is highly probable that the synthesis of nitriles from the amides of carboxylic acid and phosphorus pentoxide likewise involves an intermediate stage of N-phosphoric acids, which are cleaved by heat into free phosphoric acid and the nitrile. There is, therefore an indisputable tendency for the liberation of a mineral acid in the free state or as an acid chloride, a salt, and the like, during thermal cleavages.

A rather large number of experiments have been performed on the thermal cleavage of sulfamide and of its metallic derivatives, but we have been unable as yet to find any derivatives of sulfanic acid among the decomposition products.

The second method proposed proved to be more successful. When trichlorophosphazosulfuryl chloride, with an m.p. of 32-33°, was heated in vacuum to 118-129°, about 0.92 mol of phosphorus oxychloride per mol of the acid chloride was used in the reaction. Hence, about 91% of the acid chloride was cleaved as indicated above, only some 8% decomposing without giving off phosphorus oxychloride. It is worthy of note that the crude acid chloride of trichlorophosphazosulfuric acid undergoes no change when heated as high as 137° under the same conditions. Apparently the crude product contains something that retards decomposition. Nor does decomposition occur at ordinary pressure, even when heated to 150°. As might have been expected the reaction product was not a homogeneous substance. In all probability the monomeric sulfanyl chloride undergoes further transformations, polymerization, in particular.

Two substances (α and β) were isolated from the reaction products, in addition to the phosphorus oxychloride. Moreover, it was shown indirectly that the reaction mixture contained at least three more substances (γ, δ, and ε), although these substances have not been isolated as yet. A feature of the substance ε is that when reacted with pure benzene or gasoline containing unsaturated compounds, it produces a bright golden-yellow color, which vanishes when the solvent is driven off in vacuum and reappears when the solvent is added. This substance is readily hydrolyzed by water. The substance is volatile, with a boiling point somewhat above 100° at an 8-mm vacuum. The yield of the ε substance was very small. It is quite possible that the ε substance is formed in equilibrium when one of the products is depolymerized by heat. Appreciable quantities of the substances γ and δ are produced. Both of them are hydrolyzed very readily. Substance δ is a liquid, distilling at 7 mm at about 125°, the yield being about 15.3% of the theoretical. Substance γ is a solid that apparently cannot be distilled in vacuum, is hydrolyzed with extreme ease at a temperature of about 10°, but can be suction-filtered from an aqueous mixture at 0°. The α and β substances were isolated as such, the yields being about 24% and about 18.5% of the theoretical, respectively.

Substance α contains no hydrogen or phosphorus, its composition being N≡SOCl, its molecular weight being equivalent to (N≡SOCl)$_3$. This leads us to believe that the molecular structure of the α susbstance is represented by the following formula:
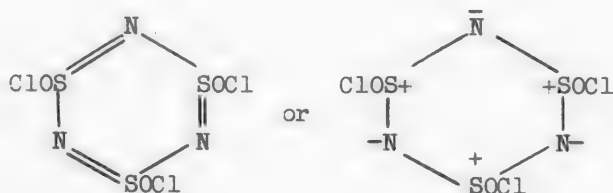
This structure is also borne out by the fact that upon hydrolysis the substance yields 6 equivalents of acid without yielding any hypochlorous acid or active chlorine. Hence, the chlorine is linked to sulfur rather than to nitrogen. Thus the α substance is most likely the first known derivative of sulfanic acid, viz: a trimer of sulfanyl chloride. It may be called 1,3,5-trichloroxo-1,3,5-trithiatriazine or, by analogy with cyanuryl chloride, sulfanuryl chloride. It is worthy of note that sulfanuryl chloride fuses at 144.5-145.5°, while cyanuryl chloride has a m.p. of 146°, and that sulfanuryl chloride sublimes just as readily as cyanuryl chloride. The extent of the analogy between sulfanuryl and cyanuryl chlorides as far as their chemical properties are concerned will be set forth below.

Sulfanuryl chloride is hydrolyzed rather slowly by water. A sample weighing about 0.2 g, mixed with 30 ml of water, was hydrolyzed completely only after 45 minutes of continuous stirring at 90°. This may be due to the negligible solubility of the substance in water, since hydrolysis takes place very quickly when alcohol is added to the mixture. When a crystal of sulfanuryl chloride is placed on Congo paper and water is dropped on it, it takes some time for a blue spot to appear, but if the water contains a little alcohol, the blue spot appears immediately. Sulfanuryl chloride does not decompose when kept above sulfuric acid in a desiccator or kept in sealed ampoules, but it does react slowly with atmospheric moisture when stored under ordinary conditions, exhibiting a faintly acid reaction after a few hours have passed, while the vessel in which it was kept is found to contain gaseous hydrogen chloride. The m.p. of sulfanuryl chloride is 144.5-145.5° without decomposition; it distils at about 270°, though distillation usually ends with an explosion. When 0.4 g of sulfanuryl chloride was distilled at atmospheric pressure, for example, about half the substance distilled before an explosion occurred that sent the distilling flask and the receiver flying in little pieces. When sulfanuryl chloride is rapidly heated on a platinum spatula it is deflagrated in a very characteristic fashion, with a blue flame. Hydrogen chloride and sulfur dioxide are liberated. When 0.4 g of sulfanuryl chloride was heated over a small flame in an upright test tube, it boiled quietly for five minutes without any outwardly apparent decomposition, but then it exploded with a bright blue flash and a loud "hiss", the test tube escaping unscathed. Sulfur was deposited on the cooler upper walls of the test tube, and the strong odor of sulfur monochloride was perceptible. Sulfanuryl chloride sublimes readily when heated in vacuum, sublimation begining at 60° at a pressure of 0.5 mm, and being very rapid at 123-130°. The melting point of the sublimed substance is the same as that of the recrystallized chloride.

Sulfanuryl chloride is readily soluble in benzene and ether. It crystallizes excellently from 85-95° petroleum ether (prepared from "overshoe" gasoline) or from benzene. It is also soluble in alcohol, but the solution turns acid at once — this probably involves the formation of an ester of sulfanuric acid. Sulfanuryl chloride reacts energetically with ammonia and with amines, both in aqueous solutions and in the absence of water. As its structural formula indicates, sulfanuryl chloride must exist as two geometrical isomers: cis with all three chlorine atoms on one side of the ring; and trans, with two chlorine atoms on one side of the ring and one on the other side. Inasmuch as the stereo structure of the α-substance is still unknown, it must be called α-sulfanuryl chloride.

The yield of the β-substance was about 18.5% of the theoretical. The elementary composition and molecular weight of the β-substance did not differ from those of the α-sulfanuryl chloride, it being a stereo isomer of the latter appar-

ently. Thus, the α- and β-substances are most likely two of the theoretically possible geometrical isomers of sulfanuryl chloride. Inasmuch as the stereo structure of the β-substance is still unknown, we must call it β-sulfanuryl chloride. The β-sulfanuryl chloride has a much lower melting point than the α isomer (145.5° for the α and 47.5° for the β) and is much more soluble in petroleum ether. For example, 1.0 g of the α compound dissolves in 100 g of petroleum ether (bp. 70-75°, from "overshoe" gasoline), while 1.0 g of the β compound dissolves in 2.5 g of the same petroleum ether at the same temperature. What is more, the β compound sublimes more easily than the α one. The β isomer deflagrates in the same way as the α isomer when heated on a platinum spatula or in a test tube. When we hydrolyzed β-sulfanuryl chloride in hot water, we noticed that some of the substance escaped with the vapor without decomposing and that hydrolysis involved an intermediate stage in which some high-melting substances were formed. β-Sulfuranyl chloride is hydrolyzed at a rate approximating that of the α compound.

The physical properties of the isomeric sulfanuryl chlorides led us to think that the α compound is the trans-sulfanuryl chloride, while the β compound is the cis-sulfanuryl chloride, but this question can be definitely settled only after a more thorough study of the physical and chemical properties of both compounds.

## EXPERIMENTAL

Thermal cleavage of trichlorophosphaszosulfuryl chloride. 0.5 mol of trichlorophosphazosulfuryl chloride (125.44 g) with a m.p. of 33° was placed in a flask for vacuum distillation, fitted with a 300-mm herringbone dephlegmator, a capillary for supplying air, and a thermometer with its bulb immersed in the substance. The air that entered the capillary was first desiccated in a Tishchenko bottle containing calcium chloride. The receiver was chilled to -20° with a freezing mixture. The flask was heated over an oil bath, first to 130°, and toward the end to 150°. The pressure within the system was maintained at 8 mm during the reaction. The reaction set in when the temperature of the bath was 130° and that of the liquid was 113°; the temperature of the vapor was 22.5°. The temperature of the bath was raised to 145° in the course of 10-15 minutes, which caused the liquid's temperature to rise to 121-122° at first and then to drop to 118.5°, after which it began to rise again when 10 minutes had elapsed. Apparently, 118.5° is the decomposition temperature of the acid chloride. Twenty minutes after the onset of the reaction the driving off of the phosphorus oxychloride increased noticeably, the vapor temperature rising to 25°, and then beginning to drop gradually. The phosphorus oxychloride usually crystallized in the receiver. The reaction was complete within 70 to 80 minutes, the end of the reaction being easily noted by the temperature of the liquid rising to 129° (at a bath temperature of 150°) and by the temperature of the vapor dropping to 21.5° (at a room temperature of 19°). The phosphorus oxychloride entrained other high-boiling reaction products, which condensed in the column and thus were not collected in the distillate. The reaction balance was as follows: residue in the flask — 53.64 g, in the column — 0.49 g, total residue — 54.13 g; theoretical yield 48.76 g. The yield of phosphorus oxychloride with a m.p. of 0.6 g totaled 67.21 g, while the losses totaled 4.10 g. If the losses are due to the phosphorus oxychloride, the overall yield of phosphorus oxychloride was 71.31 g, or 92.98% of the theoretical. Thus, the reaction follows the reaction adopted, but there is no doubt that some 8% of the trichlorophosphazosulfuryl chloride decomposes without evolving the oxychloride.

The reaction product was a transparent, faintly brownish liquid, from which rather numerous colorless crystals settled out upon cooling. Large transparent prisms settled out at room temperature; cooling to -10° caused the further settling out of numerous acicular crystals. When the crystalline deposit was suction-filtered at room temperature, most of the product left on the filter was the high-melting α compound, which is slowly hydrolyzed by water. When the crystalline deposit was suction-filtered at 0°, three substances are left on the filter, namely: the α, then the low-melting, difficultly hydrolyzable β, and finally the γ, a readily hydrolyzable solid. The quantity of suction-filtered substance left on the filter is not diminished by mixing it thoroughly with ice water, hydrolysis being very slow; but when the temperature of the mixture is raised to 10°, the γ substance is quickly hydrolyzed, the temperature rising sharply to 40-60° (if not much water is present), and the β substance fusing and passing through the filter as an oil that crystallizes upon cooling, leaving the pure α substance upon the filter. This procedure involves the hydrolysis of appreciable quantities of α and β as well. It is better, therefore, to effect separation as follows. The reaction product was left to stand for a day at room temperature, after which the crystals that settled out, containing practically all the α substance, some of the β, and some of the readily hydrolyzable γ substances, were suction-filtered and pressed out. The yield of the crude α product totaled 17-19 g. The substance was thoroughly mixed with 75 ml of ice water to get rid of the readily hydrolyzable impurities, after which the mixture was heated to 15° for 10 minutes, the product being suction-filtered and washed four times with 10 ml of water heated to 15°. After suction-filtering, the substance was immediately desiccated in a 0.5-mm vacuum above sulfuric acid at room temperature. This yielded 13.12 g of a snow-white crystalline substance that consisted of the α product with a slight trace of β. To eliminate the latter the substance was washed four times with 5-ml batches of 85-95° petroleum ether, leaving a residue of 11.92 g, or about 24% of the theoretical quantity of the α substance, with a m.p. of 141-144°. The substance was recrystallized from ten times its weight of (85-95°) petroleum ether for final purification. The substance settled out as large prisms or platelets clustered into large aggregates, with an uncorrected m.p. of 144.5-145.5°. The losses in recrystallization were negligible. See the general section for the properties of this substance.

The filtrate left after recovery of α was distilled in a 7-mm vacuum. With an oil-bath temperature of 160°, a small quantity distilled at 120-125°, the bulk passing over at 125-129°, after which distillation came to a stop, the flask contents boiling up violently at a bath temperature of 196°, though this caused no rise in pressure and nothing was distilled. The flask residue (probably the γ substance plus its decomposition products) was cooled, turning into a thick, dark-brown mass, which was not investigated any further for the moment, while the distillate (18.85 g) was a transparent lemon-yellow liquid. As the distillate was cooled, large prisms of the β substance settled out. After being allowed to stand at room temperature for a day, the distillate was chilled to 5° during the course of two hours, and the crystalline deposit was suction-filtered out. The yield was 8.15 g. To remove the readily hydrolyzable impurities, the substance was treated with 30 ml of ice water, the mixture being heated to 15° for 10-15 minutes, and the substance suction-filtered, washed three times with 10-ml batches of water heated to 15°, and immediately desiccated above sulfuric acid at room temperature and a vacuum of 0.5 mm. The substance was successively treated on a suction filter with 10, 5, and 5-ml batches of 85-95° petroleum ether, in which the β substance

is readily soluble, to get rid of the traces of the α product. Driving off the petroleum ether in vacuum left 6.05 g of crude β-sulfanuryl chloride in the flask, as large, colorless prisms with a m.p. of 42.0-43.5°.

The filtrate left after isolating the β (about 10.5 g) contained considerable β and a low-melting, readily hydrolyzable, δ substance. The filtrate was agitated with 100 ml of water to eliminate the δ substance. Most of the substance was hydrolyzed within the course of a few minutes, the residue crystallizing rapidly. It was suction-filtered after standing for 30 minutes, washed, and desiccated. This yielded another 3.00 g of β substance with a m.p. of 41-42.5°. The total yield of the crude β-sulfanuryl chloride was about 9.0 g, or about 18.5% of the theoretical. To secure an absolutely pure substance, the crude product was dissolved in as little light petroleum ether as possible, the slight quantity of the insoluble α compound being filtered out, and three-quarters of the solvent being driven off in a slight vacuum at 30-35°. As the solution was chilled, the sulfanuryl chloride settled out as large transparent prisms, up to 5 mm long, with a m.p. of 46-47°. The recrystallized substance was finally purified by sublimation in a 5-mm vacuum at 80°. The sublimed β-sulfanuryl chloride consisted of minute lustrous transparent prisms with a m.p. of 47-47.5°. The melting point quickly fell to 42-43° when it was exposed to the air.

The δ substance has not been isolated in the pure state as yet, though its yield is rather high, approximately 7.5 g, or some 15.3% of the theoretical. It is not impossible that the δ substance is a mixture of several substances.

When the crude α or β substance was desiccated in vacuum desiccators, the vaseline on the inside of the ground-glass surfaces was turned into a dark-brown, malodorous mass — these substances apparently contained some volatile impurities that reacted with the vaseline. This phenomenon was not observed when the pure α and β substances were kept in vacuum desiccators.

When we washed out the herringbone dephlegmator with benzene after the reaction, we noticed that the benzene was colored a bright golden-yellow. Driving off the benzene in vacuum left behind a nearly colorless oily liquid, which colored benzene a bright golden-yellow again when dissolved in it. A much fainter color was observed when the crude decomposition product and the distillate containing the β and δ products were dissolved in benzene. The color disappeared instantly when a drop of water was added. The distilled phosphorus oxychloride did not produce this color with benzene.

The reaction products thus include a very small quantity of still another substance ε, it seems, which colors benzene a bright golden-yellow that vanishes when the benzene is driven off. The same color is produced by gasoline that contains unsaturated compounds. If there are no unsaturated compounds in the gasoline, the contents of the column dissolve in it without any coloration.

Analysis of α-sulfanuryl chloride. All the analyses were performed in the usual manner.

0.0496 g subs.: 0.0002 g $H_2O$; 0.0503 g subs.: 0.0002 g $H_2O$; 0.2048 g subs.: 8 50 ml 0.5 $\underline{N}$ alkali; 0.3014 g AgCl; 0.2212 g substance: 9.15 ml 0.5 $\underline{N}$ alkali; 0.3228 g AgCl; 0.1021 g subs.: 0.2437 g $BaSO_4$, 0.0928 g subs.: 0.2216 g $BaSO_4$. 0.1538 g substance: 15.65 ml 0.1 $\underline{N}$ acid; 0.1583 g substance: 16.15 ml 0.1 $\underline{N}$ acid; 0.3390 g substance; 16.16 g benzene: Δt 0.367°; 0.4397 g subs.: 16.16 g benzene: Δt 0.481°. Found %; $\underline{H}$ 0.04, 0.04; Cl 36.39, 36.08; $\underline{S}$ 32.78, 32.80; $\underline{N}$ 14.26, 14.29. Acid equivalent found upon hydrolysis: 6.072, 6.054. $\underline{M}$ 292.5, 289.6. $(NSOCl)_3$. Calculated %. $\underline{H}$ 0.00; Cl 36.35; $\underline{S}$ 32.87; $\underline{N}$ 14.39. Calculated acid equivalent upon hydrolysis 6.000; $\underline{M}$ 292.56.

Analysis of β-sulfanuryl chloride.  All the analyses were performed in the usual manner.

0.0643 g substance:  0.0001 g $H_2O$;  0.0662 g substance:  0.0001 g $H_2O$; 0.1012 g subs. 0.1485 g AgCl;  0.1016 g subs.:  0.1486 g AgCl.  0.0867 g subs. 0.2061 g $BaSO_4$;  0.0830 g substance:  0.1980 g $BaSO_4$;  0.2564 g substance: 26.30 ml 0.1 $\underline{N}$ acid;  0.2579 g substance:  26.55 ml 0.1 $\underline{N}$ acid;  0.2743 g substance:  11.20 ml 0.5 $\underline{N}$ alkali;  0.3213 g substance:  13.25 ml 0.5 $\underline{N}$ alkali;  0.1248 g substance;  15.51 g benzene: Δt 0.145°;  0.2517 g substance;  15.51 g benzene: Δt 0.288°.  Found %:  H 0.02, 0.02;  Cl 36.31, 36.19;  S 32.65, 32.76;  N 14.37, 14.42.  Acid equivalent found upon hydrolysis:  5.967, 6.027;  $\underline{M}$ 285.2, 289.7. $(NSOCl)_3$.  Calculated %:  H 0.00; Cl 36.35;  S 32.87;  N 14.39.  Calculated acid equivalent upon hydrolysis 6.000;  $\underline{M}$ 292.56.

## SUMMARY

It has been shown that the thermal cleavage of trichlorophosphazosulfuryl chloride results in the formation of phosphorus oxychloride and products of the transformation of sulfanyl chloride.

Two trimers of sulfanyl chloride have been isolated from these products, and it has been shown that these trimers are most likely two theoretically possible stereo isomers of sulfanuyrl chloride or 1,3,5-trichloroxo-1,3,5-trithiatriazine.  The properties of the two isomeric sulfanuryl chlorides are described.

## LITERATURE CITED

[1]  A. V. Kirsanov and Yu. M. Zolotov, Sci. Trans. Dnepropetrovsk Metallurgical Inst., No. XX, 62.

[2]  W. Traube, Ber. 25, 2472 (1892); 26, 607 (1893).

[3]  A. Hantzsch and A. Holl, Ber., 34, 3430 (1901).

[4]  A. V. Kirsanov, J.Gen.Chem., 22, 88 (1952).

[5]  A. V. Kirsanov and Yu. M. Zolotov, Sci. Trans. Dnepropetrovsk Metallurgical Inst., No. XX, 29;  P. Baumgarten and J. Marggraff, Ber., 64, 1582 (1931).

# TRICHLOROPHOSPHAZOSULFURYL CHLORIDE

## A. V. Kirsanov

Research on the reaction of sulfamic acid with phosphorus pentachloride is of considerable interest, inasmuch as we may hope to secure the hitherto unknown sulfamyl chloride in this reaction, or else some more highly complicated product related to sulfamyl chloride.

The reaction of sulfamic acid and phosphorus pentachloride has been investigated by F. Ephraim and M. Gurewitsch [1], who found that one molecule of sulfamic acid reacts with two molecules of phosphorus pentachloride, the second molecule of the phosphorus pentachloride decomposing (at 90-100°) into chlorine and phosphorus trichloride, the latter combining with the sulfamyl chloride to form the stable binary compound $ClSO_2NH_2 \cdot PCl_3$.* Ephraim and Gurewitsch were unable to cleave this latter compound into its components. Inasmuch as Ephraim and Gurewitsch fail to supply adequately substantiated data in the experimental section of their paper in support of the composition and structure of the product of the reaction between sulfamic acid and phosphorous pentachloride, and inasmuch as there are weighty reasons [2] for not trusting the accuracy of Ephraim's and Gurewitsch's findings, we resolved to make our own study of the reaction of sulfamic acid and phosphorus pentachloride. This study indicated that most of the data reported by Ephraim and Gurewitsch were wrong and that the compound $ClSO_2NH_2 \cdot PCl_3$ either is nonexistent or has not been synthesized as yet, the compound to which Ephraim and Gurewitsch assigned this composition and structure being altogether different.

As our experiments have shown, finely pulverized sulfamic acid readily reacts with powdered phosphorus pentachloride at the temperature of a boiling water bath, exactly two molecules of phosphorus pentachloride reacting with one molecule of sulfamic acid. Three molecules of hydrogen chloride and one molecule of phosphorus oxychloride are evolved in the reaction. The overall reaction is therefore: $NH_2SO_2OH + 2PCl_5 \rightarrow 3HCl + POCl_3 + SO_2NPCl_4$. The reaction sets in faster and comes to an end faster when carbon tetrachloride is present.

Ephraim and Gurewitsch assert that chlorine is evolved during the reaction. That is true, chlorine actually being liberated, but in very minute quantities, viz: 0.35% of the theoretical, based on the reaction proposed by Ephraim and Gurewitsch. It should be added that this quantity of chlorine is very much less than that evolved when trichloroacetamide is reacted with phosphorus pentachloride or when pure phosphorus pentachloride is heated to 100-110° for approximately the same length of time [3]. Hence, the evolution of chlorine undoubtedly has no direct relation to the main reaction.

According to Ephraim and Gurewitsch, the reaction product left after the phosphorus oxychloride was removed consisted of "a thick, dark-brown liquid that did not crystallize at room temperature." This is untrue, the reaction product actually being a wholly transparent, colorless, rather mobile liquid, which crystallized quickly at room temperature and melted at 23° (maximum, with the thermometer bulb immersed in the liquid). Ephraim and Gurewitsch apparently used highly impure initial substances, which may also be the reason

*The reaction is as follows: $NH_2SO_2OH + 2PCl_5 \rightarrow HCl + POCl_3 + ClSO_2NH_2 \cdot PCl_3$.

for their asserting that phosphorus trichloride was formed in the reaction.

The composition of the reaction product leads us to think that its structure is that of $ClSO_2N=PCl_3$, <u>i.e.</u>, it is trichlorophosphazosulfuryl chloride. This supposition is borne out by determination of its molecular wt., by the analytical findings — determination of hydrogen, sulfur, chlorine, and phosphorus — and by the fact that hydrolysis of the substance yields seven acid equivalents (with thymolphthalein) as follows:

$$ClSO_4N=PCl_3 \xrightarrow{+H_2O} 4HCl + HOSO_2ONH_4 + H_2HPO_4.$$

The assertion of Ephraim and Gurewitsch that phosphorus acid is produced by hydrolysis is incorrect, only phosphoric acid being formed.

The yield of the crude acid chloride, with a m.p. of 23°, was 99.45% of the theoretical, based on the sulfamic acid entering into the reaction, but this product contains a rather large percentage of some low-melting impurities, which can be readily eliminated by suction-filtering, evidently as a eutectic with the acid chloride. The acid chloride thus prepared consists of snow-white crystals with a m.p. of 33° (thermometer bulb in the liquid), the yield of the pure product being about 75% of the theoretical. The melting point was raised to 35-36° after several recrystallizations from petroleum ether, all moisture being excluded (thermometer bulb in the liquid). The composition of the products with melting points of 33° and 36° is the same, however, the crude acid chloride having nearly the same composition as the refined preparations. Hence, the "impurities" have the same composition as the acid chloride, and are either its polymers or isomers.

It should be stressed that the stated yields and composition of the reaction products are secured only when pure and absolutely dry sulfamic acid and pure phosphorus pentachloride are used (it is best to use freshly prepared phosphorus pentachloride and not more than 2.06 mols of the latter per mol of the sulfamic acid). When too great an excess of phosphorus pentachloride is employed, the yield of the solid product is diminished, the melting point of the crude acid chloride drops sharply, and the elementary composition of the crude product changes. When commercial products are used as the initial substances, there is a great difference between the composition of the crude acid chloride and the product suction-filtered after crystallization, while the yield of the pure acid chloride is reduced appreciably. These are probably the reasons for the inaccurate data secured by Ephraim and Gurewitsch.

Trichlorophosphazosulfuryl chloride is readily soluble in benzene, ether, and carbon tetrachloride and slightly soluble in petroleum ether, its solubility rising somewhat when the latter is hot. Trichlorophosphazosulfuryl chloride is extremely hygroscopic, deliquescing rapidly in the air. When the crude product, with a m.p. of 23°, is mixed with water at room temperature, it reacts violently, with a characteristic noise, within a few seconds. The suction-filtered acid chloride, with a m.p. of 33°, reacts somewhat more quietly with water, tiny particles rapidly "running" over the surface of the water. Hydrolysis is much slower at 0°. The reaction of the acid chloride with a concentrated aqueous solution of ammonia or with gaseous ammonia is very violent. The acid chloride reacts as readily with alcohols, amines, and phenols The acid chloride underwent no change, at least in the course of 16 months, when kept in a sealed ampoule. The acid chloride may be distilled in vacuum, provided the quantity is not too large (up to 5 g) and distillation is rapid.

Its b.p. is 135-140° at 7 mm.

Even rapid distillation, however, is accompanied by partial decomposition, the melting point of the distilled product always being lower than that of the initial substance. When 5 g of the acid chloride with a m.p. of 33° was distilled, for instance, we secured 4.0 g of acid chloride with a m.p. of 21°.

When the acid chloride is distilled slowly, it undergoes a highly interesting decomposition, which has been reported in the previous paper (p. 93.).

The high chemical activity of trichlorophosphazosulfuryl chloride and its availability are grounds for expecting that this acid chloride may serve as the starting point for the synthesis of diversified derivatives of sulfamic and phosphazosulfuric acids.

<div align="center">EXPERIMENTAL</div>

Experiments using 0.05 to 0.1 mol of sulfamic acid were performed in order to make a quantitative determination of all the products of the reaction between sulfamic acid and phosphorus pentachloride. In the preparative synthesis of trichlorophosphazosulfuryl chloride we used up to 2 mols of sulfamic acid. Typical experiments of both types are described below.

Reaction of sulfamic acid with phosphorus pentachloride. 0.1 mol (9.71 g) of thoroughly pulverized anhydrous sulfamic acid and 0.2 mol (41.65 g) of freshly prepared phosphorus pentachloride were placed in a 100-ml round-bottomed flask. The phosphorus pentachloride was weighed out and charged into the flask in a dry chamber. The flask was closed with an inclined reflux condenser, filled with brine at a temperature of -17°. The outlet end of the condenser was connected to three absorbing vessels in series, with tubes reaching to above the surface of the liquid. The first absorber was filled with 300 ml of a 1.0N solution of alkali, the second and third each containing 100 ml of the 1.0N solution of alkali. The absorbers were chilled with ice water. The flask containing the reaction mixture was immersed in a boiling water bath. The evolution of hydrogen chloride set in at once, as was evident from the "current" in the liquid within the first absorber. Phosphorus oxychloride, entrained by the current of hydrogen chloride, soon began to condense within the reflux condenser, a small amount of sublimed phosphorus pentachloride depositing on the inner tube of the condenser. (Should the phosphorus pentachloride be deposited on the neck of the flask, an attempt must be made to wash it off with the refluxed oxychloride, turning the flask to get at all the deposit, or else the flask must be plunged more deeply into the bath.) The reaction mixture began to liquefy within an hour, becoming wholly liquid after two hours, and the reaction came to an end after two hours and a half had elapsed. The reaction product was a colorless, transparent, mobile liquid containing a small quantity of minute crystals. It was qualitatively determined in a special test that these were crystals of unreacted sulfuric acid. The weight of the reaction products totaled 38.33 g, i.e., including the escaping hydrogen chloride, phosphorus oxychloride, phosphorus pentachloride, and 13.03 g of chlorine. The phosphorus oxychloride was driven off over a water bath with an "isolated" vacuum and a receiver that was chilled to -20°. The distillate consisted of 13.4 g of phosphorus oxychloride with a m.p. of 0.8°, the m.p. of a fusion sample being likewise 0.8° (thermometer bulb in the liquid). The residue weighed 24.43 g, indicating that the loss of phosphorus oxychloride during evacuation was 0.05 g and making the total yield of phosphorus oxychloride 13.9 g, or 90.61% of the theoretical, not allowing for

any that escaped with the hydrogen chloride during the reaction. The residue in the flask was suction-filtered through a tiny weighed filter fitted with a porous glass plate in order to recover the sulfamic acid, which was washed with anhydrous benzene. The sulfamic acid recovered weighed 0.32 g, or 3.30% of the quantity charged into the flask. In the titration of this sulfamic acid we used 3.4 ml of a 1.0N alkali solution, equivalent to 0.33 g, or 3.40% of the quantity charged into the flask. Hence, the yield of the crude trichlorophosphazosulfuryl chloride was 24.11 g, or 96.12% of the theoretically possible, or 99.45% based on the reacted sulfamic acid. The recovery of the pure product and its properties are described below, under the preparative method used for synthesizing the acid chloride.

The phosphorus pentachloride deposited within the condenser was quickly removed with a special spatula and weighed, after which the condenser was washed with 250.0 ml of water to which 50.0 ml of a 1.0N alkali solution had been added. The phosphorus pentachloride scraped off the condenser was cautiously added to this solution, and the excess alkali was titrated back with a 1.0N acid solution containing thymolphthalein. The phosphorus pentachloride recovered weighed 0.62 g, or 1.49% of the amount placed in reaction, while 0.69 g, or 1.66% of the quantity placed in the reaction, was found by titration (26.76 ml of a 1.0N alkali solution, i.e., 23.24 ml of 1.0N alkali solution was required to neutralize the phosphoric and hydrochloric acids).

The contents of all three absorbers were transferred quantitatively to a 1-liter flask, and the contents of the latter were brought up to 1000 g. 500 g of this solution was used to titrate the active chlorine with a 0.1 N solution of hyposulfite, 3.52 ml of the latter being consumed, which was the equivalent of 0.0125 g of free chlorine. Hence a total of 0.0250 g of free chlorine was evolved during the reaction, or 0.175% of the theoretical quantity, based on the phosphorus pentachloride, that is, much less than the percentage that Wallach found was evolved [3] when phosphorus pentachloride was reacted with trichloroacetamide or when pure phosphorus pentachloride was heated to 100-110° for about the same length of time. If we go by the Ephraim and Gurewitsch equation, the free chlorine evolved totaled 0.35% of the theoretical quantity.

The other half of the solution was used to determine the acidity, but first 100-g batches of the solution were boiled for 2-3 hours with reflux condensers to decompose the hypochlorous acid. 16.20 ml of a 1.0N acid solution containing thymolphthalein was required per 100 g of the solution. Therefore the solution contained 0.338 equivalent of acid or, allowing for the hydrogen chloride remaining within the apparatus (derived volume of about 120 ml), 0.343 equivalent. Of this total 0.0276 equivalent must have resulted from the phosphorus oxychloride entrained by the hydrogen chloride (as computed from the difference between the theoretical yields of the acid chloride and the yield of the phosphorus oxychloride, which totaled 5.51%), while 0.0319 equivalent must have resulted from the phosphorus pentachloride entrained by the hydrogen chloride (based on the difference between 100% and the overall yield of the acid chloride and the per cent of phosphorus pentachloride found in the condenser, which totaled 2.28%). Thus, 0.283 equivalent of hydrogen chloride was formed in the main reaction (ignoring the percentage of free chlorine because of its minuteness), or 97.59% based on the reacted sulfamic acid.

Reaction balance sheet. 0.1 mol of sulfamic acid was used, of which 0.9665 mol entered into the reaction; 0.2 mol of phosphorus pentachloride

was used. The yield of the crude acid chloride was 96.12% of the theoretical. The yield of the crude acid chloride was 99.45% based on the reacted sulfamic acid. The yield of phosphorus oxychloride totaled 0.9061 mol. The acids formed when the gaseous reaction products reacted with water totaled 0.343 equivalent. 0.060 equivalent of acids must have been formed from the phosphorus oxychloride and pentachloride entrained with the hydrogen chloride. The hydrogen chloride evolved during the main reaction totaled 0.283 equivalent. The hydrogen chloride evolved was 97.59%, based on the reacted sulfamic acid. The free chlorine evolved totaled 0.35% of the theoretical, based on the Ephraim and Gurewitsch equation.

These figures definitely prove that the principal reaction involved in the interaction of sulfamic acid with phosphorus pentachloride follows the equation given above.

Preparative synthesis of trichlorophosphazosulfuryl chloride. 2 mols (184.2 g) of sulfamic acid, dried at 100° in vacuum and pulverized, and 4.12 mols (858 g) of pulverized phosphorus pentachloride were placed in a 2-liter round-bottomed flask fitted with a reflux condenser. 100 ml of anhydrous carbon tetrachloride was added to the mixture, and the flask was held down in a boiling water bath. The evolution of hydrogen chloride set in soon. Within 30 minutes the reaction mixture began to liquefy noticeably, turning into a transparent colorless liquid within two hours. An appreciable quantity of phosphorus pentachloride was deposited within the condenser. The reaction ended after two and a half hours had elapsed, and after the reaction mixture had cooled, it was suction-filtered to remove the minute quantity of unreacted sulfamic acid (about 0.5 g).

The phosphorus oxychloride and the carbon tetrachloride were driven off in vacuum, over a boiling water bath toward the end of the process. In one of the tests, run without adding any carbon tetrachloride, we secured 284 g, or 92.5% of the theoretical, of phosphorus oxychloride with a m.p. of +0.8°. The residue left after the phosphorus oxychloride had been driven off — the crude trichlorophosphazosulfuryl chloride — was a nearly colorless, transparent liquid that rapidly crystallized when chilled into a dense radiating mass of crystals saturated with liquid. The yield of the crude product was 497.7 g, or 99.2% of the theoretical based on the sulfamic acid. The preparation fused readily, the last crystal vanishing at 23° (thermometer bulb in the liquid).

The next day the product was suction-filtered and thoroughly pressed out. This yielded 325 g, or 65% of the theoretical, of trichlorophosphazosulfuryl chloride as a snow-white crystalline mass with a m.p. of 33° (maximum, with the thermometer bulb in the liquid; supercooling to 29°). The filtrate was chilled to -10°, a seed crystal was added, and the whole was suction-filtered one hour later. This yielded 51 g, or about 10% of the theoretical, of the acid chloride with a m.p. of 32°. The total yield of solid product with a m.p. of about 33° was 376 g, or 75% of the theoretical. A little more of the solid acid chloride could be secured by even deeper chilling of the filtrate, which was a nearly colorless oily liquid.

All the operations involved in suction-filtering the acid chloride should be performed in a dry cabinet or in a well-ventilated laboratory on extremely cold days. The acid chloride decomposes very slowly in air when the outside temperature is below -20° and there is a draft in the laboratory. The acid chloride may also be suction-filtered and pressed out "under rubber", but

then the top layer of the substance is darkened by contact with the rubber.

The acid chloride was recrystallized (in a dry cabinet) from petroleum ether that had a b.p. of 75-85°, prepared from "overshoe" gasoline, all of whose unsaturated compounds had been eliminated by repeated treatment with sulfuric acid. The trichlorophosphazosulfuryl chloride crystallized from the petroleum ether as colorless needles with a m.p. of 35-36°. It is best to keep the acid chloride in the molten state, as the product is decomposed much more rapidly by atmospheric moisture when the container is opened or when it is taken from the desiccator, if it is in the shape of individual crystals.

Analyses of trichlorophosphazosulfuryl chloride. One of the decisive factors in proving that the products of the interaction of phosphorus pentachloride and sulfamic acid had the structure of trichlorophosphazosulfuryl chloride is the presence or absence of hydrogen in it. The hydrogen was determined by the usual combustion method.*

It is quite obvious that this percentage of hydrogen can only be due to the accidental entrace of atmospheric moisture, so that the structure suggested for the substance by Ephraim and Gurewitsch is indisputably wrong.

The phosphorus, the sulfur, the chlorine, and the acid equivalent produced during hydrolysis were determined by the customary methods after a sample of the substance had been hydrolyzed by an excess of 0.5N solution of sodium hydroxide. The nitrogen was determined after a sample of the substance had been hydrolyzed in water, followed by hydrolysis in concentrated hydrochloric acid. The molecular weight was determined cryoscopically in benzene. In the subjoined analyses for P, S, and Cl, the first two figures refer to the crude acid chloride, the third and fourth to the preparation with a m.p. of 32-33°, and the fifth and sixth to the preparation with a m.p. of 35-36°. In the molecular weight determinations the first two figures refer to the preparation with a m.p. of 32-33°, and the third and fourth to the preparation with a m.p. of 35-36°.

0.3513 g, 0.3625 g, 0.4002 g, 0.3091 g, 0.3416 g and 0.3523 g substance: 0.1565 g, 0.1620 g, 0.1771 g, 0.1367 g, 0.1508 g and 0.1558 g $Mg_2P_2O_7$. 0.2709 g, 0.2485 g, 0.2520 g, 0.2170 g, 0.2361 g and 0.2219 g substance: 0.2508 g, 0.2304 g, 0.2342 g, 0.2016 g, 0.2192 g and 0.2062 g $BaSO_4$. 0.1429 g, 0.1381 g, 0.1545 g, 0.1420 g, 0.1388 g and 0.1325 g substance: 0.3240 g, 0.3136 g, 0.3516 g, 0.3237 g, 0.3162 g and 0.3017 g $AgCl$. 0.2610 g, 0.2653 g, 0.2574 g, 0.2645 g, 0.2549 g and 0.2674 g substance: 10.25 ml, 10.45 ml, 10.20 ml, 10.50 ml, 10.10 ml, 10.60 ml 0.1 N acid. 0.3774 g, 0.3796 g, 0.3663 g, 0.3667 g, 0.3895 g and 0.3897 g substance: 10.65 ml, 10.70 ml, 10.25 ml, 10.25 ml, 10.90 ml and 10.90 ml 1.0 N alkali. 0.0986 g, 0.1593 g, 0.1156 g and 0.1828 g substance. 18.0 g benzene: Δt 0.112°, 0.184°, 0.132° and 0.211°. Found %: P 12.41, 12.46, 12.33, 12.32, 12.29, and 12.32; S 12.72, 12.73, 12.76, 12.76, 12.75 and 12.76; Cl 56.08, 56.15, 56.33, 56.37, 56.33 and 56.32; N 5.50, 5.52, 5.55, 5.56, 5.55 and 5.55. Found: acid equiv. in hydrolysis: 7.08, 7.07, 7.02, 7.01, 7.02 and 7.02; M 247.4, 244.2, 247.5 and 243.8.

$ClSO_2NPCl_3$. Calculated %: P 12.37; S 12.78; Cl 56.54; N 5.59. Calculated: acid equivalent in hydrolysis 7.00. M 250.92.

## SUMMARY

It has been shown that a satisfactory yield of trichlorophosphazosulfuryl chloride is produced by reacting phosphorus pentachloride with sulfamic acid.

*0.1232 g subs.: 0.18 mg $H_2O$; 0.1103 g subs.: 0.24 mg $H_2O$. Found %: H0.016, 0.024.

It has been shown that the findings by Ephraim and Gurewitsch to the effect that the reaction of sulfamic acid with phosphorus pentachloride yields a binary compound of phosphorus trichloride and sulfamyl chloride are incorrect, and that all data concerning that compound should be deleted from textbooks and the reference literature.

The properties and the method of preparation of trichlorophosphazosulfuryl chloride are described.

## LITERATURE CITED

[1]   F. Ephraim and M. Gurewitsch, Ber., 43, 138 (1910).

[2]   A. V. Kirsanov and Yu. M. Zolotov, "Synthesis of free imidosulfamide and its properties," J. Gen. Chem., 21, 1790 (1951).

[3]   O. Wallach and Th. Huth, Ber., 8, 317 (1875).

# THE REACTIVITY OF ORGANIC HYDROXIDES OF MERCURY

## THE REACTION OF PHENYLMERCURY HYDROXIDE WITH PHENOLS

### S. M. Labuzov

Dimroth [1] has shown that phenols are mercurated very easily, yielding ortho and para substitution products.  The reaction is such that almost always we obtain dimercurated, and sometimes trimercurated, phenols, into addition to the monomercurated one.  M. M. Koton and T. M. Zorina [2] have shown that when diphenylmercury and dinaphthylmercury are reacted with phenols, monomercurated, dimercurated, and trimercurated derivatives of the phenols are produced.  Koton and Chernov [3] have found that similar products are formed when tolyl derivatives of mercury are reacted with the phenols.  Koton [4] made a study of the reaction of mercury derivatives of the $C_6H_5HgAc$ and also secured monomercurated, dimercurated, and trimercurated phenol derivatives.

It is known that hydroxides of organometallic compounds are highly reactive, so that the reaction of organic hydroxides of mercury with the phenols must be of considerable interest.

The present paper is a study of the reaction of phenylmercury hydroxide with the following phenols:  p-nitrophenol, o-nitrophenol, 2,4-dinitrophenol, trinitrophenol, p-chlorophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol, resorcinol, and pyrogallol.  The reaction was carried out at 130° with and without solvents present.  As might have been expected, the experiments in which alcohol was used resulted in the evolution of metallic mercury.

In our study of the reaction of phenylmercury hydroxide with phenols we have found that phenols may be readily mercurated by introducing an ArHg radical, using phenylmercury hydroxide;  dimercurated phenol derivatives constituted the bulk of the reaction products, with trimercurated derivatives occurring in some instances.  When the reaction conditions were milder (100°), monomercurated compounds were produced.  It should be stressed that mercuration via $C_6H_5HgOH$ is easier than with $(C_6H_5)_2Hg$ and its functional derivatives; this inference follows from the fact that under identical conditions $(C_6H_5)_2Hg$ yields mono- and dimercurated derivatives, while $C_6H_5HgOH$ yields nothing but dimercurated derivatives.

## EXPERIMENTAL

All our experiments on the reaction of phenylmercury hydroxide with the phenols were made by heating a mixture of the substances to 130° in sealed glass ampoules.

1.  Phenylmercury hydroxide and p-nitrophenol.  0.3 g of p-nitrophenol was used for 0.3 g of phenylmercury hydroxide.  Heating lasted 3 hours.  Two principal products were recovered from the (yellow) reaction mixture by successively treating it with aqueous alcohol, alcohol, and benzene.  The excess

p-nitrophenol (0.21 g) was recovered from the aqueous alcohol solution. The principal reaction product was a heavy, yellow, infusible powder (0.2640 g) that was insoluble in organic solvents.

0.05 g substance:  2.86 ml  0.1 N.  NH$_4$CNS.  Found %:  Hg 57.20. (C$_6$H$_5$Hg)$_2$C$_6$H$_2$(OH)NO$_2$.  Calculated %:  Hg 57.96.

This compound is therefore the dimercurated derivative of p-nitrophenol.

2.  Phenylmercury hydroxide and o-nitrophenol. The experimental conditions and the subsequent processing of the reaction mixture were the same as in the case of the p-nitrophenol.  The aqueous alcoholic solution yielded 0.268 g of the yellow crystals of the unreacted o-nitrophenol, with a m.p. of 41-42°.  The alcohol yielded 0.1148 g of the colorless crystals of the unreacted hydroxide.

The residue consisted of 0.1618 g of a heavy yellow powder that was infusible up to 300°, which was purified and then analyzed for mercury.

0.05 g substance:  2.82 ml 0.1 N.  NH$_4$CNS.  Found %:  Hg 56.23. (C$_6$H$_5$Hg)$_2$C$_6$H$_2$(OH)NO$_2$.  Calculated %:  Hg 57.96.

Hence, this compound is the dimercurated derivative of o-nitrophenol.

3.  Phenylmercury hydroxide and 2,4-nitrophenol.  The experimental conditions and the subsequent processing of the reaction mixture were the same as in the case of the p-nitrophenol.

A total of 0.1328 g of crystals with a m.p. of 109-111° was recovered from the aqueous alcoholic solution.  This represented the excess 2,4-dinitrophenol.  A total of 0.1014 g of yellowish crystals with a m.p. of 126-127° was recovered from the alcoholic solution.  This was a mixture of the excess 2,4-dinitrophenol and phenylmercury hydroxide.  The residue was the yellow-orange powder of the dimercurated derivative, which was insoluble and infusible up to 250°.  The impurities were eliminated from the compound by dissolving it in alkali and precipitating it with CO$_2$.

0.05 g substance: 2.72 ml 0.1 N NH$_4$CNS. Found %: Hg 54.40. (C$_6$H$_5$Hg)$_2$C$_6$H(OH)(NO$_2$)$_2$.  Calculated %: Hg 54.50.

As we see from the analysis, this compound is the dimercurated derivative of 2,4-dinitrophenol.

4.  Phenylmercury hydroxide and 2,4-dinitrophenol.  This experiment was run at 100°, the processing of the reaction mixture being the same as that for the p-nitrophenol.

A total of 0.221 g of crystals with a m.p. of 111-112° — the excess 2,4-dinitrophenol — was recovered from the aqueous alcohol.  A total of 0.2108 g of the yellow crystals of the monomercurated derivative of 2,4-dinitrophenol was recovered from the alcohol.

0.05 g substance: 2.123 ml 0.1 N NH$_4$CNS. Found %: Hg 42.46. C$_6$H$_5$HgC$_6$H$_2$(OH)(NO$_2$)$_2$. Calculated %: Hg 43.69.

The residue contained 0.0135 g of an insoluble and infusible, pale-yellow powder — the dimercurated derivative.

0.0135 g substance: 0.70 ml 0.1 N NH$_4$CNS. Found %: Hg 54.23. (C$_6$H$_5$Hg)$_2$C$_6$H(OH)(NO$_2$)$_2$. Calculated %: Hg 54.50.

5.  Phenylmercury hydroxide and 2,4-dinitrophenol.  This experiment was

run with alcohol present, the reaction mixture being processed as in the case of the p-nitrophenol.

5.1% of free mercury was found. 0.1100 g of an insoluble and infusible dark-brown powder was recovered.

0.05 g substance: 2.66 ml 0.1 N NH$_4$CNS. Found %: Hg 53.20.
$(C_6H_5Hg)_2C_6H(OH)(NO_2)_2$. Computed %: Hg 54.50.

Hence, this compound is the dimercurated derivative of 2,4-dinitrophenol.

6. Phenylmercury hydroxide and trinitrophenol. The experimental conditions and the processing of the reaction mixture were the same as those used for the p-nitrophenol.

A total of 0.2119 g of yellow crystals with a m.p. of 98° – apparently the unreacted picric acid with a trace of the phenylmercury hydroxide – was recovered from the aqueous alcoholic solution. The alcoholic solution yielded 0.2925 g of a nearly colourless powder with a m.p. of 158°.

0.05 g substance: 1.96 ml 0.1 N NH$_4$CNS. Found %: Hg. 39.20.
$C_6H_5HgC_6H(OH)(NO_2)_3$. Computed %: Hg 39.60.

Hence, this compound is the monomercurated derivative of picric acid.

7. Phenylmercury hydroxide and p-chlorophenol. The experimental conditions and the processing of the reaction mixture were the same as in the case of the p-nitrophenol.

In this experiment 6.53% of free mercury was evolved. 0.1868 g of an infusible product that was insoluble in organic solvents was obtained.

0.05 g substance: 11.608 ml 0.05 N Na$_2$S$_2$O$_3$. Found %: Hg 58.04.
$(C_6H_5Hg)_2C_6H_2(OH)Cl$. Computed %: Hg 58.23.

The analytical data indicate that this insoluble powder was the dimercurated derivative of p-chlorophenol.

8. Phenylmercury hydroxide and 2,4-dichlorophenol. The experimental conditions and the processing of the reaction mixture were the same as in the case of the p-nitrophenol.

A total of 0.1486 g of the excess 2,4-dichlorophenol, with a m.p. of 47°, was recovered from the aqueous alcoholic solution. The insoluble and infusible product totaled 0.1904 g.

0.05 g substance: 11.056 ml 0.05 N Na$_2$S$_2$O$_3$. Found %: Hg 55.28
$)C_6H_5Hg)_2C_6H(OH)Cl_2$. Computed %: Hg 55.94.

The analysis indicates that this was the dimercurated derivative of 2,4-dichlorophenol.

9. Phenylmercury hydroxide and 2,4,6-trichlorophenol. The experimental conditions and the processing of the reaction mixture were the same as in the case of the p-nitrophenol.

0.1 g of the trichlorophenol, with a m.p. of 79°, was recovered from the aqueous alcoholic solution. A total of 0.141 g of crystals with a m.p. of 86° – apparently a mixture of the trichlorophenol and the phenylmercury hydroxide – was recovered from the alcoholic solution. The residue, which was insoluble and fused at 300° (with decomposition) and totaled 0.2102 g, was the dimercurated derivative of 2,4,6-trichlorophenol.

0.05 g substance: 10.584 ml 0.05 N Na$_2$S$_2$O$_3$. Found %: Hg 52.92.
$(C_6H_5Hg)_2C_6H(OH)Cl_2$. Computed %: Hg 53.30.

10.  **Phenylmercury hydroxide and resorcinol.**  The experimental conditions and the processing of the reaction mixture were the same as in the case of the p-nitrophenol.

Brown crystals with a m.p. of 107° − the excess resorcinol − were recovered from the aqueous alcoholic solution.  The residue was 0.2320 g of a dark-red infusible substance.

0.05 g substance: 3.19 ml 0.1 N $NH_4CNS$.  Found %: Hg 63.80 $(C_6H_5Hg)_3C_6H(OH)_2$.  Calculated %: Hg 64.03.

Hence, the insoluble residue was the trimercurated derivative of resorcinol.

11.  **Phenylmercury hydroxide and pyrogallol.**  The experimental conditions and the processing of the reaction mixture were the same as in the case of the p-nitrophenol.

A total of 28.34% of free mercury was evolved.

12.  **Phenylmercury hydroxide and pyrogallol.**  This experiment was performed in ethyl alcohol.

A total of 41.43% of free mercury was evolved in the experiment.

### SUMMARY

1.  It has been established, for the first time, that phenylmercury hydroxide is able to mercurate the phenols.

2.  The principal reaction products in the mercuration of the phenols were the dimercurated derivatives.

3.  It has been shown that phenylmercury hydroxide is more highly reactive than other organomercury compounds in the mercuration of phenols.

### LITERATURE CITED

[1]  Dimroth, Ber., 35, 2032, 2853 (1902).

[2]  Koton and Zorina, J. Gen. Chem. 17, 1220 (1947).

[3]  Koton and Chernov, J. Gen. Chem. 19, 2104* (1949).

[4]  Koton, J. Gen. Chem. 19, 730,734** (1949).

*See C.B. English translation, p. a-575.
**See C.B. English translation, p. 709.

# THE REACTION OF ORTHODITOLYLMERCURY WITH ORGANIC ACIDS

## I. A. Chernov

It has been shown in an earlier paper [1] that para and orthoditolyl-mercury react with organic acids, forming acyl derivatives of the $CH_3C_6H_4HgOCOR$ type. It was found that orthoditolylmercury is highly reactive. Only the reactions of orthoditolylmercury with some acids (formic, acetic, isovaleric, lactic, oxalic, and salicylic acids) have been explored. We were interested in making a more thorough study of these reactions with various organic acids.

Further study was undertaken of the reactions of orthoditolylmercury with the following monobasic saturated acids: butyric, myristic, palmitic, and stearic acids, as well as with the following halogen substitution derivatives of monobasic saturated acids: chloroaecetic, bromoacetic, and trichloroaectic acids. Of the monobasic acids, the reactions of orthoditolyl-mercury with the following acids were investigated: succinic, glutaric, adipic, azelaic, maleic, fumaric, and tricarballylic acids. Of the aliphatic hydroxy acids, tartaric and citric acids were tested, and of the aromatic acids, benzoic, gallic, sulfosalicylic and phthalic acids.

Orthoditolylmercury generally reacts with acids as follows: $(CH_3C_6H_4)_2 Hg +$ + $RCOOH \longrightarrow CH_3C_6H_5 + RCOOHgC_6H_4CH_3$. The resulting acyl derivatives were isolated in the pure state, and the conditions governing their formation, their melting points, and their solubility in various solvents were established. The acyl derivatives of saturated monobasic acids are white crystalline substances with low melting points (below 90°) that are freely soluble in organic solvents.

It should be noted that orthoditolylmercury reacts very readily (at room temperature) with the halogen substitution derivatives of monobasic saturated acids, yielding crystalline compounds of the following general formula: $CH_2HalCOOHgC_6H_4CH_3$. Tracing the reactions of orthoditolylmercury with dibasic acids is likewise of interest. Succinic acid, for example, yields disubstituted acyl derivative of the $CH_3C_6H_4HgOCO(CH_2)_2COOHgC_6H_4CH_3$ type, whereas the following representatives of the homologous series: glutaric, adipic, and azelaic acids, as less reactive even under more severe conditions (100°, heating for 3 hours), yield nothing but monosubstituted derivatives of the $CH_3C_6H_4HgOCO(CH_2)_nCOOH$ type. Reactions with maleic and fumaric acids are no less interesting. Maleic acid, which is a cis isomer, reacts more energetically with orthoditolylmercury, forming a disubstituted product, whereas fumaric acid yields only a monosubstituted product.

Tartaric acid, which is a hydroxy derivative of succinic acid, also yields a disubstituted acyl derivative. Citric acid behaves differently, yielding a monosubstituted derivative. Orthoditolylmercury reacts normally with aromatic acids: monobasic benzoic and gallic acids, yield monobasic acyl

derivatives, while sulfosalicylic and phthalic acids yield disubstituted derivatives.

## EXPERIMENTAL

All the tests were run under the conditions set forth above [1]. The mercury content was determined in the usual manner, the Whitmore and Sobatzki method [2] being used only for the halogen-substitution acids.

Orthoditolylmercury and n-butyric acid. 0.2 g of orthoditolylmercury and 1 ml of butyric acid were reacted together at room temperature for 96 hours. As the aqueous solution cooled, a white precipitate settled out that was soluble in ether, alcohol, acetone and benzene, and dissolved when heated in water. The m.p. of orthotolylmercury butyrate is 86-87°. The yield was 0.125 g (63.1% of the theoretical).

0.03 g substance: 1.569 ml 0.1 N NH₄CNS. Found %: Hg 52.30. $C_{11}H_{14}O_2Hg$. Calculated %: Hg 53.00.

Orthoditolylmercury and myristic acid. 0.2 g of orthoditolylmercury and 0.14 g of myristic acid were heated together for 3 hours to 100°. The white waxlike deposit was heated gently with alcohol, after which aqueous alcohol was added and the precipitate was filtered out. Recrystallization from acetone yielded a white powder that was soluble in ether and benzene, soluble when gently heated in alcohol and acetone, and insoluble in water. The m.p. of orthotolylmercury myristate is 71°. The yield was 0.1 g (37% of the theoretical):

0.03 g substance: 1.151 ml 0.1 N NH₄CNS. Found %: Hg 38.37. $C_{21}H_{34}O_2Hg$. Calculated %: Hg 38.68.

Orthoditolylmercury and palmitic acid. 0.2 g of orthoditolylmercury and 0.15 g of palmitic acid were heated to 100° for 3 hours. The resulting light-brown hyaline mass was treated with warm alcohol, after which aqueous alcohol was added and the resultant precipitate was filtered out. Recrystallization from alcohol yielded a white powder that was soluble in ether, acetone, and benzene, soluble when heated in alcohol and insoluble in water. The m.p. of orthotolylmercury palmitate is 69-70°. The yield was 0.14 g (49% of the theoretical).

0.05 g substance: 1.82 ml 0.1 N NH₄CNS. Found %: Hg 36.40. $C_{23}H_{38}O_2Hg$. Calculated %: Hg 36.70.

Orthoditolylmercury and stearic acid. 0.2 g of orthoditolylmercury was heated with 0.1 g of stearic acid for 3 hours. The resulting greenish-brown mass was treated with warm alcohol, the resulting solution being poured into a beaker, where it solidified into a dense mass. After the latter had been recrystallized from aqueous alcohol, the precipitate was filtered out and desiccated. The resulting light-brown powder was soluble in ether and benzene, soluble when heated in alcohol and acetone, and insoluble in water. The m.p. of orthotolylmercury stearate is 59°. The yield was 0.18 g (59% of the theoretical).

0.03 g substance: 1.026 ml 0.1 N NH₄CNS. Found %: Hg 34.20. $C_{25}H_{42}O_2Hg$. Calculated %: Hg 34.31.

Orthoditolylmercury and chloroacetic acid. Reacting 0.2 g of orthoditolylmercury with 0.1 g chloroacetic acid for 96 hours at room temperature yielded a grayish-white precipitate. The later was dissolved in water, the solution being poured out into cold water. The faintly colored resulting precipitate was filtered out and dessicated. The precipitate was soluble in ether, alcohol, acetone, and benzene, and (when heated) in water. The m.p. of orthotolyl-

mercury chloroacetate is 81°.  The yield was 0.16 g (80% of the theoretical).

0.1 g substance: 10.50 ml 0.05 N $Na_2S_2O_3$.  Found %: Hg 52.47.  $C_9H_9O_2ClHg$.  Calculated %: Hg 52.09.

Orthoditolylmercury and bromoaectic acid.  0.2 g of orthoditolylmercury was reacted with 0.1 g of bromoacetic acid for 96 hours at room temperature, resulting in the formation of a white precipitate.  The latter was treated with water, the solution being poured out into water.  The precipitate that settled out was soluble in ether, acetone, and benzene, and (when heated) in alcohol and water.  The m.p. of orthotolylmercury bromoacetate is 82-83°.  Its yield was 0.19 g (84.8% of the theoretical).

0.1 g substance: 9.50 ml 0.05 N $Na_2S_2O_3$.  Found %: Hg 47.52. $C_9H_9O_2BrHg$.  Calculated %: Hg 46.69.

Orthoditolylmercury and trichloroacetic acid.  0.2 g of orthoditolyl-mercury was reacted with 0.1 g of trichloroacetic acid for 96 hours at room temperature, resulting in the formation of a brown powder.  The latter was treated with water, the solution being poured out into cold water.  Filtration and desiccation yielded a white powder that was soluble in ether, benzene, and acetone, and (when gently heated) in alcohol, but was only slightly soluble in water.  The m.p. of orthotolylmercury trichloroacetate is 112-114°.  Its yield was 0.19 g (80.2% of the theoretical).

0.1 g substance: 9.02 ml 0.05 N $Na_2S_2O_3$.  Found %: Hg 45.08. $C_9H_7O_2Cl_3Hg$.  Calculated %: Hg 44.18.

Orthoditolylmercury and succinic acid.  0.2 g of orthoditolylmercury was heated with 0.07 g of succinic acid in the presence of one drop of water to 100° for 1 hour.  The resultant white precipitate was heated in alcohol, the flask contents then being poured out into cold water.  The precipitate thrown down was filtered out, desiccated, and heated with acetone.  The precipitate was insoluble in water or in the following organic solvents:  ether, alcohol, acetone, or benzene.  The m.p. of orthoditolylmercury succinate is 200° with decomposition.  The yield was 0.06 g (16.4% of the theoretical).

0.02 g substance: 1.15 ml 0.1 N $NH_4CNS$.  Found %: Hg 57.53. $C_{18}H_{18}O_4Hg_2$.  Calculated %: Hg 57.38.

Orthoditolylmercury and glutaric acid.  0.2 g of orthoditolylmercury was heated with 0.08 g of glutaric acid in the presence of one drop of water to 100° for 3 hours.  The resultant light-brown precipitate was heated in water, the flask contents then being transferred to cold water.  The resulting precipitate was filtered out and then recrystallized from acetone.  The m.p. of orthotolyl glutarate       is       105-106°.  The yield was 0.04 g (17.5% of the theoretical).  The substance was insoluble in ether or water, but soluble in acetone and (when heated) in alcohol and benzene.

0.02 g substance: 0.942 ml 0.1 N $NH_4CNS$.  Found %: Hg 47.10. $C_{12}H_{14}O_4Hg$.  Calculated %: Hg 47.46.

Orthoditolylmercury and adipic acid.  0.2 g of orthoditolylmercury was heated with 0.1 g of adipic acid in the presence of one drop of water to 100° for 3 hours.  The fused product was treated with hot water and filtered out.  A precipitate of orthotolylmercury adipate, with a m.p. of 94-96°, settled out of the solution.  The yield was 0.15 g (65.9% of the theoretical).  The precipitate was insoluble in water or ether, though soluble when heated in alcohol, acetone, and benzene.

0.05 g substance: 2.332 ml 0.1 N $NH_4CNS$. Found %: Hg 46.64. $C_{13}H_{16}O_4Hg$. Calculated %: Hg 45.95.

Orthoditolylmercury and azelaic acid. 0.2 g of orthoditolylmercury was heated with 0.12 g of azelaic acid in the presence of one drop of water to 100° for 3 hours. The fused resulting light-brown mass was gently heated with aqueous alcohol and filtered out, yielding a light-brown product that dissolved when heated in water, alcohol, acetone, and benzene, and was insoluble in ether. Orthotolylmercury azelate has a m.p. of 85-87°. Its yield was 0.16 g (64% of the theoretical).

0.05 g substance: 2.061 ml 0.1 N $NH_4CNS$. Found %: Hg 41.22. $C_{16}H_{22}O_4Hg$. Calculated %: Hg 41.91.

Orthoditolylmercury and maleic acid. 0.2 g of orthoditolylmercury and 0.08 g of maleic acid were heated together with one drop of water for 3 hours at 100°. The fused resulting light-brown mass was gently heated in aqueous alcohol and filtered out yielding a white precipitate that was insoluble in water or these organic solvents: either, alcohol, acetone, and benzene. The m.p. of orthoditolylmercury maleate is 186-188° with decomposition. The yield was 0.15 g (41.2% of the theoretical).

0.05 g substance: 2.856 ml 0.1 N $NH_4CNS$. Found %: Hg 57.11. $C_{18}H_{16}O_4Hg_2$. Calculated %: Hg 57.54.

Orthoditolylmercury and fumaric acid. 0.2 g of orthoditolylmercury was heated with 0.08 g of fumaric acid and one drop of water to 100° for 3 hours. The fused resulting light-brown mass was heated gently in aqueous alcohol. Filtration yielded a light-pink product that was insoluble in water or in these organic solvents: ether, alcohol, acetone, and benzene. The m.p. of orthotolylmercury fumarate is 184-185° with decomposition. The yield was 0.17 g (80% of the theoretical).

0.05 g substance: 2.447 ml 0.1 N $NH_4CNS$. Found %: Hg 48.95. $C_{11}H_{10}O_4Hg$. Calculated %: Hg 49.33

Orthoditolylmercury and tricarballyic acid. 0.2 g of orthoditolylmercury was heated with 0.1 g of tricarballylic acid and one drop of water to 100° for 3 hours. The dark precipitate was treated with cold water and filtered out. Treatment with hot alcohol yielded a light-brown precipitate that was insoluble in water, ether, alcohol, acetone, or benzene. The m.p. of orthotolylmercury tricarballylate is 199-200° with decomposition. The yield was 0.08 g (32.8% of the theoretical).

0.3 g substance: 1.276 ml 0.1 N $NH_4CNS$. Found %: Hg 42.54. $C_{13}H_{14}O_6Hg$. Calculated %: Hg 42.99.

Orthoditolylmercury and tartaric acid. 0.2 g of orthoditolylmercury was heated with 0.1 g of tartaric acid and one drop of water to 100° for 1 hour. The resultant white precipitate was treated with cold water and filtered out. Subsequent processing with hot water yielded a white substance that was insoluble in ether, alcohol, acetone, benzene, or water. The m.p. of orthoditolylmercury tartrate is 191° with decomposition. The yield was 0.16 g (40% of the theoretical).

0.03 g substance: 1.621 ml 0.1 N $NH_4CNS$. Found %: Hg 54.04. $C_{18}H_{18}O_6Hg_2$. Calculated %: Hg 54.87.

Orthoditolylmercury and citric acid. 0.2 g of orthoditolylmercury was heated with 0.2 g of citric acid and one drop of water to 100° for 3 hours.

The resulting gray precipitate was treated with cold water and filtered out. This yielded a white precipitate that was insoluble in water or in the following organic solvents: ether, alcohol, acetone, and benzene. The m.p. of orthotolylmercury citrate is 150-152° with effervescence. The yield was 0.12 g (52.2% of the theoretical).

0.05 g substance: 2.29 ml 0.1 N $NH_4CNS$. Found %: Hg 45.80. $C_{13}H_{14}O_7Hg$. Calculated %: Hg 45.63.

Orthoditolylmercury and benzoic acid. 0.2 g of orthoditolylmercury was heated with 0.1 g of benzoic acid to 100° for 1 hour. The resulting gray precipitate was treated with cold water and filtered out. The resulting tacky mass crystallized after some time had elapsed, turning into a white powder that was soluble in organic solvents. The m.p. of orthotolylmercury benzoate is 58-60°. The yield was 0.1 g (46.3% of the theoretical).

0.05 g substance: 2.395 ml 0.1 N $NH_4CNS$. Found %: Hg 47.90. $C_{14}H_{12}O_2Hg$. Calculated %: Hg 48.61.

Orthoditolylmercury and gallic acid. 0.2 g of orthoditolylmercury was heated with 0.12 g gallic acid and one drop of water to 100° for 1 hour. The resulting gray powder was gently heated with water and filtered out. This yielded a gray powder that was soluble when heated in alcohol and in acetone and was insoluble in water, ether, or benzene. The m.p. of orthotolylmercury gallate is 133° with decomposition. Its yield was 0.17 g (70.5% of the theoretical).

0.05 g substance: 2.155 ml 0.1 N $NH_4CNS$. Found %: Hg 43.10. $C_{14}H_{12}O_5Hg$. Calculated %: Hg 43.55.

Orthoditolylmercury and sulfosalicylic acid. 0.2 g of orthoditolylmercury was heated to 100° for 1 hour with 0.15 g of sulfosalicylic acid and one drop of water. The fused resultant light-brown mass was treated with cold water and filtered out, yielding light-brown rhombic crystals that were soluble in ether, acetone, and benzene, and (when heated) in water and in alcohol. The m.p. of orthoditolylmercury sulfolsalicylate is 101-102°. Its yield was 0.17 g (40.7% of the theoretical).

0.03 g substance: 2.531 ml 0.1 N $NH_4CNS$. Found %: Hg 50.62. $C_{21}H_{18}O_6SHg_2$. Calculated %: Hg 50.20.

Orthoditolylmercury and phthalic acid. 0.2 g of ditolylmercury was heated to 100° for 1 hour with 0.1 g of phthalic acid and one drop of water. The fused resulting light-brown mass was treated with alcohol and filtered out, after which it was retreated with hot alcohol. This yielded a lustrous white powder that was soluble when heated in alcohol or benzene and was insoluble in water or ether. The m.p. of orthoditolylmercury phthalate is 174-175°. The yield was 0.15 g (38.5% of the theoretical).

0.03 g substance: 1.59 ml 0.1 N $NH_4CNS$. Found %: Hg 53.00. $C_{22}H_{18}O_4Hg_2$. Calculated %: Hg 53.69.

SUMMARY

1. A study has been made of the reactions of orthoditolylmercury with various organic acids.

2. It has been shown that these reactions yield acyl derivatives of the general formulas $CH_3C_6H_4HgOCOR$ and $CH_3C_6H_4HgOCORCOOHgC_6H_4CH_3$ which are crystalline substances with definite melting points, most of which are soluble

in organic solvents.

LITERATURE CITED

[1]  I. A. Chernov, J. Gen. Chem. 20, 325*(1950).

[2]  Whitmore, Sobatzki, J. Am. Chem. Soc., 55, 1128 (1933).

*See C.B. English translation, p. 345.

POLYMERIZATION – DEPOLYMERIZATION

## VII.   THE STRUCTURE OF THE TETRAMER OF ISOBUTYLENE

### Ya. M. Slobodin and E. M. Markova

The polymerization of isobutylene with sulfuric acid was investigated long ago by Butlerov [1], who secured the dimer and trimer forms. Isobutylenes of higher molecular weight were prepared by Lebedev [2], who polymerized butylene with silicates.  It was found that the mean molecular weight of the polymers depended upon the polymerization temperature (Lebedev and Borgman [3]) as well as upon the nature of the silicates (Slobodin [4]).

The polymerization of isobutylene may be represented satisfactorily enough by Whitmore's diagram, in which a carbon ion is formed as an intermediate product [5].  Among the dimers and trimers of isobutylene forms have been found that were predicted by this diagram and are in full agreement with it.

The structure of the tetraisobutylenes has been unknown up to the present time.  Using Whitmore's diagram to explain their formation, we might expect the three isomeric tetraisobutylenes represented below to be formed, with the first form predominating (Petrov [6]):
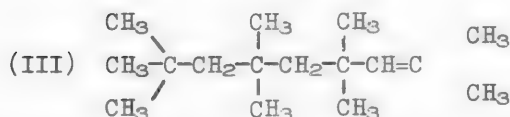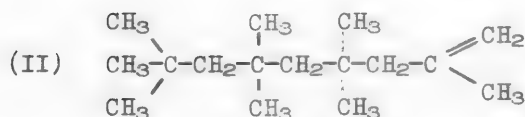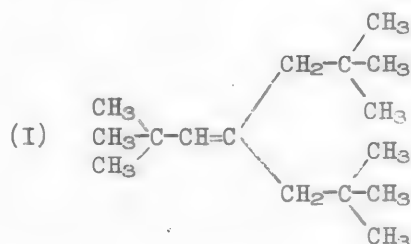


We employed ozonolysis to investigate the structure of the tetramers of isobutylene in the present research, besides studying their Raman spectra. The chemical and physical research methods yield identical results.  The Raman spectra were also photographed in the laboratory of the Institute of Physics of the University of Leningrad (headed by Prof. E. F. Gross).

It was found that the spectra of the tetrameric forms of isobutylene contain two double-bond frequencies, 1637 and 1650 $cm^{-1}$, after they had been separated from the other polymeric forms.

The tetramer was separated in vacuo into two fractions with b.p. of 89° at 3 mm and 92-94° at the same pressure. The spectra of these fractions each contained two double-bond frequencies: 1634 and 1652 $cm^{-1}$ in the spectrum of the first tetramer, and 1629 and 1645 $cm^{-1}$ in the spectrum of the second.

These findings indicate that the tetramer of isobutylene is a mixture of at least two isomeric forms with the same kind of double bond.

There is no doubt that vacuum fractionation without an efficient enough separatory column cannot separate the mixture into the individual hydrocarbons. The difference between the spectra of these fractions indicates that one isomer predominates in one fraction, and the other isomer in the other.

The Raman spectra are convincing proof that neither of these two fractions contains any appreciable percentages of hydrocarbons that are symmetrical disubstituted or trisubstituted ethylenes, since these latter hydrocarbons all possess a double-bond frequency of the order of 1670 $cm^{-1}$. All the isomeric tetramers of isobutylene in these fractions must contain the $-C\begin{smallmatrix}\diagup CH_2 \\ \diagdown CH_3\end{smallmatrix}$ group.
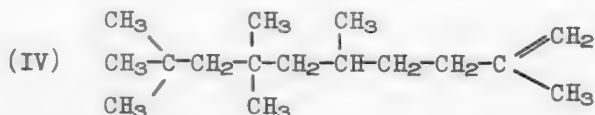
This group is covered by Structure (II).

It should also be noted that the frequencies of 1629 and 1634 $cm^{-1}$ are too low. A check proved that this is not due to any error of measurement.

Both of the tetramer fractions were then ozonolyzed, the following compounds being found to be the principal decomposition products in each case: a ketone with the molecular weight of 230, which corresponds to the empirical formula $C_{15}H_{30}O$ ($\underline{M}$=226), and formic acid. No acetone was found, but a small quantity of trimethylacetic acid was detected.

The results of ozonolysis thus confirm that the bulk of the isobutylene tetramer consists of a form corresponding to the structure (II). The presence of trimethylacetic acid is evidence of the presence in the tetramer of spectrographically indeterminable percentages of a form corresponding to the structure (I). The percentage of this form may be estimated from our data as approximately 10%. The same quantitative ratio follows from a comparison of the yields of the trimethylacetic acid. The tetramer forms have no isomer corresponding to the structure (III).

As we have stated above, the tetramer of isobutylene is a mixture of at least two isomeric hydrocarbons with the same kind of double bond. Judging by the intensity of the frequencies, we may assume that the percentages of these isomers are about the same. Though the above findings clearly indicate the structure of one of these isomers, various surmises may be ventured as to the structure of the others. Another isomer may be the addition product of a molecule of isobutylene and its trimer on the "end-to-end" principle, which would correspond to the structure (IV):

$$(IV) \quad CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-\underset{\overset{CH_3}{|}}{CH}-CH_2-CH_2-C\begin{smallmatrix}\diagup CH_2 \\ \diagdown CH_3\end{smallmatrix}$$

A different distribution of the methyl groups in the tetramer is not impossible, as indicated by the research of Petrov [7] on the destructive hydrogenation of polyisobutylenes under pressure. At the present time, we do not rule out the possibility that these and other forms are present.

Still, the adoption of any of the foregoing structures for the second tetramer of isobutylene does not explain the reason for the appreciable drop in the frequency of the double bond. We incline to relate this phenomenon to the presence of "rotational isomerism" [8].

It should be said that examination of the Raman spectra indicates the presence of a similar phenomenon for the pentamers and still higher polymers of isobutylene. We have made a study of these problems in conjunction with Prof. E. F. Gross and published them in a separate report [8].

## EXPERIMENTAL

The tetramer of isobutylene was prepared by polymerizing isobutylene above floridin, chilling with ice water being used. Vacuum fractionation yielded a fraction with a b.p. of 107-112° at 17 mm.

The tetramer was then separated into fractions with a b.p. of 87-89° at 3 mm, 92-94° at 3 mm, and 102-105° at 3 mm, though only the first two fractions were analyzed.

Fraction with a b.p. of 87-89° (3 mm). $d_4^{20}$ 0.7932; $n_D^{20}$ 1.44807; $\gamma^{20}$ 26.44 dynes/cm. Found: $\underline{MR}_D$ 75.53; P 644; M 229. $C_{16}H_{32}F$. Calculated: $\underline{MR}_D$ 75.62; P 647; M 224.

Raman spectrum (frequencies in $cm^{-1}$): 210(5), 533(3), 573(1), 688(4W) 724(10), 747(8), 772(4), 825(4), 874(3), 937(1), 990(1), 1005(3), 1034(4), **1115(3)**[*] 1177(2), 1205(5), 1253(4), 1290(3), 1323(3), 1402(4), **1407**(8) 1453(5), 1471(3), **1634**(6), **1652**(6), 2490(1), 2779(8), 2904(3), 3074(4).

Fraction with a b.p. of 92-94° (3 mm). $d_4^{20}$ 0.7938; $n_D^{20}$ 1.44927; $^{20}$ 24.99 dynes/cm. Found: $\underline{MR}_D$ 75.53; $\underline{P}$ 631; $\underline{M}$ 222. $C_{16}H_{32}$ Calculated: $\underline{MR}_D$ 75.62; $\underline{P}$ 647; $\underline{M}$ 224.

Raman spectrum (frequencies in $cm^{-1}$): 243(2), 310(1), 462(2), 553(1), 557(3), 583(3), 588(2), 618(2), 628(3), 678(4 W), 722(8), 744(10), 767(4), 821(4), 869(3), 889(4 W), 976(1), 1029(3), 1067(4), **1113**(3), 1167(2), 1199(5), 1204(4), 1276(3), 1314(3), **1403**(4 W), 1444(10), 1467(5), **1629**(3), **1645**(10W), 2490(1), 2528(8), 2779(3), 2977(4), **3080**(4).

Ozonolysis of the tetramer. Both fractions were ozonated. We cite the results of only one test, inasmuch as practically identical results were secured with both fractions.

We used 8.8 g of the substance and 20 ml of anhydrous chloroform in ozonation. The ozone was passed through at the rate of 15 liters per hour at -70°. When saturation with ozone was complete, the chloroform was driven off at a low vacuum. The ozonide was decomposed by boiling it with water, decomposition being extremely slow. There were two layers in the flask after the reaction was over. The upper oily layer was separated, vacuum-distilled, and analyzed. The yield was 5.6 g.

0.1410 g substance: 0.4133 g $CO_2$; 0.1651 g $H_2O$. Found %: C 79.93; H 13.01; $\underline{M}$ 230. $C_{15}H_{30}O$. Calculated %: C 79.65; H 13.27; $\underline{M}$ 226.

---

[*]Here and subsequently, bold face numbers relate to the group $-C\overset{CH_2}{\underset{CH_3}{\diagdown}}$

The bottom, aqueous layer was neutralized with potash until its re-
action was faintly alkaline, and the neutral products were extracted with
ether. A test for acetone with 2,4-dinitrophenylhydrazine was negative.
Driving off the ether left 0.2 g of the substance, which was treated with
freshly-prepared silver oxide. The reaction products were diluted with
water and thoroughly boiled, and the excess silver oxide was filtered out.
Evaporating the filtrate yielded only a small quantity of a formate, all of
which decomposed when evaporated.

The alkaline solution, which contained salts of organic acids, was
acidulated with dilute sulfuric acid. The formic acid was determined in a
separate test by the calomel method. Recalculated for the total solution,
the formic acid was found to total 1.17 g, whi h agrees with the amount of
the ketone $C_{15}H_{30}O$ formed. The acidulated solution was extracted with ether,
the ether solution being desiccated with calcium chloride. After the ether
had been driven off, the acid residue was kept in a vacuum desiccator above
a solid alkali to eliminate the formic acid. An acid with a m.p. of 28-32°
crystallized out, this being the m.p. of trimethylacetic acid. A total of
0.18 g of the crystalline acid was collected, the silver salt being prepared
from this total without purifying it. Found % Ag: 53.33%. $C_5H_9O_2Ag$. Cal-
culated %: Ag 51.67. The excessive percentage of silver in the salt is
due to incomplete elimination of the formic acid.

## SUMMARY

1. It has been shown that the principal constitutent of the tetramer
of isobutylene is 2,4,4,6,6,8,8-heptamethylnonene-1. Isomers with other
arrangements of the methyl groups may also be present.

2. It has been found that only minor quantities of 2,2,6,6-tetramethyl-
4-neopentylheptene-3, which ought to be the major constitutent of the tetramer
of isobutylene according to Whitmore's diagram, are actually formed. Its per-
centage in the reaction product may be estimated at about 10%.

3. We have not found the third tetramer of isobutylene called for by
Whitmore's diagram — 2,4,4,6,6,8,8-heptamethylnonene-2.

## LITERATURE CITED

[1] A. M. Butlerov, Jour. Russ. Chem. Soc. 5, 9, 187, 302 (1872); 8,
279, 351 (1875); 9, 38 (1876); 11, 197 (1879); 14, 199 (1882).

[2] S. V. Lebedev and G. G. Koblyansky, Jour. Russ. Chem. Soc. 61, 2176
(1930).

[3] S. V. Lebedev and Yu. A. Borgman, J.Gen.Chem. 5, 1595 (1935).

[4] Ya. M. Slobodin, J.Applied Chem. 8, 35 (1935).

[5] F. Whitmore, Chem. Eng. News, 26, 688 (1948); F. Whitmore,
Homeyer, J. Am. Soc., 54, 3435 (1932).

[6] A. D. Petrov. Synthesis and isomeric conversions of aliphatic
hydrocarbons. USSR Acad. Sci. Press (1947).

[7] A. D. Petrov, Proc. USSR Acad. Sci. 64, 349 (1949).

[8] E. F. Gross, K. V. Nelson, and Ya. M. Slobodin, Proc. USSR Acad.
Sci. 75, 697 (1950).

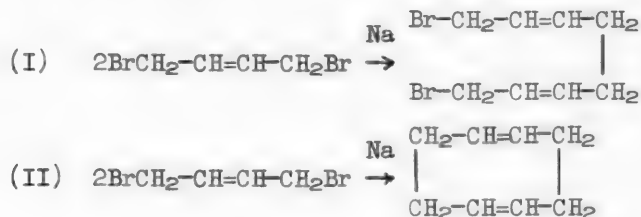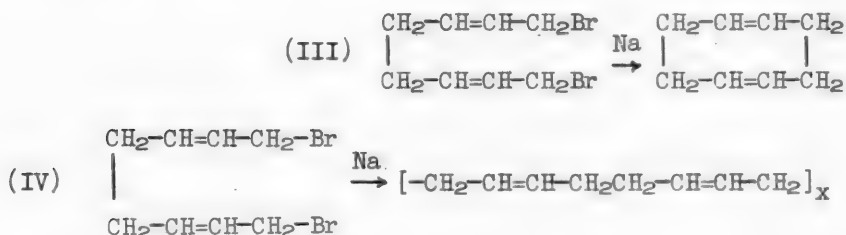## VIII.   THE ACTION OF METALLIC SODIUM ON 1,4-DIBROMOBUTENE-2

### Ya. M. Slobodin and N. M. Vinokurova

The present paper reports on a study of the products formed by the action of metallic sodium on 1,4-dibromobutene-2.

Dehalogenation may be imagined to occur in accordance with the following equations:

$$(I) \quad 2BrCH_2\text{-}CH=CH\text{-}CH_2Br \xrightarrow{Na} \begin{array}{l} Br\text{-}CH_2\text{-}CH=CH\text{-}CH_2 \\ | \\ Br\text{-}CH_2\text{-}CH=CH\text{-}CH_2 \end{array}$$

$$(II) \quad 2BrCH_2\text{-}CH=CH\text{-}CH_2Br \xrightarrow{Na} \begin{array}{l} CH_2\text{-}CH=CH\text{-}CH_2 \\ | \qquad\qquad | \\ CH_2\text{-}CH=CH\text{-}CH_2 \end{array}$$

The 1,8-dibromoctadiene-2,6 formed in Equation (I) may in turn react with sodium, yielding cyclic and aliphatic products:

$$(III) \quad \begin{array}{l} CH_2\text{-}CH=CH\text{-}CH_2Br \\ | \\ CH_2\text{-}CH=CH\text{-}CH_2Br \end{array} \xrightarrow{Na} \begin{array}{l} CH_2\text{-}CH=CH\text{-}CH_2 \\ | \qquad\qquad | \\ CH_2\text{-}CH=CH\text{-}CH_2 \end{array}$$

$$(IV) \quad \begin{array}{l} CH_2\text{-}CH=CH\text{-}CH_2\text{-}Br \\ | \\ CH_2\text{-}CH=CH\text{-}CH_2\text{-}Br \end{array} \xrightarrow{Na} [\text{-}CH_2\text{-}CH=CH\text{-}CH_2CH_2\text{-}CH=CH\text{-}CH_2]_x$$

The end product of the reaction ought to be cyclooctadiene in Equations (II) and (III). Reaction (IV) should lead to the formation of a high-molecular linear polymer of butadiene, in which all the butadiene molecules are linked together at their 1 and 4 carbon atoms. As we know, a polymer form of this kind cannot be produced by straight polymerization.

Turning to the probability that the products set forth above are formed and bearing in mind the structural chemical relationships and the strain existing in the end products, we must assume that it is hardly possible for cyclooctadiene to be formed in Equation (II), owing to the high order of the reaction.

It seemed that the dibromide formed in Equation (I) could react via either Equation (III) or Equation (IV) when dehalogenated further. We know, however, that the formation of ring systems is a rather complicated process. The facts known at the present time often contradict the strain theory. Thus a three-membered ring, which possesses the maximum strain, is formed more easily than other ring systems. It is harder for the less-strained four-membered ring to be formed. It is often impossible to produce rings with many members by dehalogenating dihalogen derivatives.

In the 1,8-dibromooctadiene-2,6 we investigated, ring-closure ought to convert it into a cyclooctadiene free from strain, but the great length of the chain and the presence of two double bonds make the probability of the end carbon atoms coming close together after the two bromo atoms have been split off extremely small, so that the eight-membered ring cannot be closed [1].

Study of the products of the debromination of 1,4-dibromobutene-2 by metallic sodium in anhydrous ether indicated that only aliphatic hydrocarbons in which the number of carbon atoms is a multiple of four are formed. We recovered hydrocarbons with eight and twelve carbon atoms. High-molecular polymer forms were also found. Splitting off the bromine is accompanied by redistribution of the hydrogen. The dimer and trimer forms are proton acceptors, so that they are transformed into octadiene and dodecatriene, respectively. The high-molecular form is thought to be a proton donor, so that it should exhibit an increased unsaturation.

Hydrogenating the dimer form by the Lebedev method [2] indicated that the substance adds two molecules of hydrogen, the first one being added very much faster than the other. The break in the hydrogenation curve is located at about 50% added hydrogen. Normal octane is formed as the result of hydrogenation.

The molecular refraction of octadiene does not display any exaltation, which is evidence that no system of conjugated double bonds is present. This is also borne out by the inability of the hydrocarbon to react with maleic anhydride.

The Raman spectrum of octadiene exhibits two double-bond frequencies: 1635 and 1654 $cm^{-1}$, of identical intensity. The presence of two frequencies is proof that the double bonds are unequal. The presence of the 1415 and 3080 $cm^{-1}$ frequencies in the spectrum leads us to believe that our octadiene contains the $CH_2=CH-$ group. This agrees with the double-bond frequency of 1635 $cm^{-1}$, which can refer only to this group in our compound.

The frequency of 1451 $cm^{-1}$ and the presence of the frequencies of 997, 1370, and 2854 $cm^{-1}$ in the spectrum indicate that the octadiene contains a methyl group, which agrees with the double-bond frequency of 1654 $cm^{-1}$, corresponding to the group $CH_3-CH=CH-$.

The foregoing indicates that the resulting octadiene has the structure of $CH_2=CH-CH_2-CH_2-CH_2-CH=CH-CH_3$.

Returning to the hydrogenation of this hydrocarbon, we may add that the course of the hydrogenation curve is like that of the hydrogenation curves of mixtures of mono- and symmetrical di-substituted ethylenes, which were exhaustively studied by Lebedev [3] (see drawing).
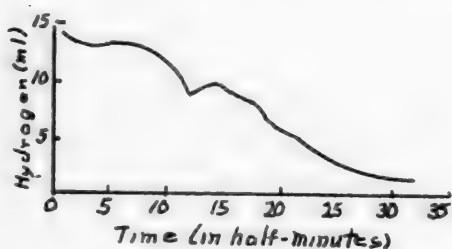


Thus, the dehalogenation of 1,8-dibromooctadiene-2,6 involves an allyl rearrangement only at one end of the chain. The reason for this may be that polarization results in the establishment of changes of opposite sign at the ends of the eight-carbon-atom complex produced by debromination. One part of these complexes is a proton acceptor and is converted into octadiene, while the other part

is a proton donor, so that it becomes more highly unsaturated and is readily polymerized to high-molecular products.

A similar state of affairs prevails in the trimer fraction, which has the empirical formula of $C_{12}H_{18}$ and contains three double bonds.

## EXPERIMENTAL

1,4-Dibromobutene-2 was prepared from technical butadiene by the Thiele method [4]. The m.p. of the bromide was 52-53° after freezing and crystallization.

A solution of the bromide in absolute ether was placed in a large vessel and metallic sodium in the shape of 0.5 mm-diameter wire was added in several batches. About 1.5 liters of the ether were used for 500 g of the bromide. To make sure that the solution always contained a fresh sodium surface, small batches were added daily until the total sodium exceeded the calculated quantity by 10-15%. In some instances the addition of the initial portions caused the mixture to heat up. After the vessel had cooled down, it was allowed to stand at room temperature. The end of the reaction was indicated by the solution failing to give a positive Beilstein test for halogen. The reaction lasted from one to three months, depending upon the quantity of bromide used. As a rule, the solution turned brownish by the end of the reaction. We noticed that increasing the concentration of the bromide slowed the reaction down, while sunlight accelerated it. A total of 3000 g of the bromide was processed. After the reaction was over the ether solution was separated from the precipitate, and the ether was driven off. The residual oil was distilled at a low vacuum in a current of carbon dioxide. The residue consisted of a brownish, vaselinelike polymer. The distilled fraction had a b.p. of 60-65° at 80 mm.

The yield of the low-boiling hydrocarbon did not exceed 10%. The crude hydrocarbon was distilled over metallic sodium, the following fractions being collected:

1) 52-115° - 7.9%; 2) 115-128° - 15.4%; 3) 123-126° - 43.5%; 4) 126-132° - 14.0%; 5) 132-220° - 16.9%; and 6) losses and residue - 2.3%.

The hydrocarbon with a b.p. of 123-126° was the major constituent of the debromination products.

$d_4^{20}$ 0.7576; $n_D^{20}$ 1.43542; $\gamma^{20}$ 22.92 dynes/cm. Found: $MR_D$ 37.91; P 318; M 110. $C_8H_{14}F_2$. Calc. $MR_D$ 38.21; P 324; M 100.

Raman spectrum (frequencies in $cm^{-1}$): 238 (1), 378 (1), 471 (1), 526 (1), 571 (1), 634 (1), 753 (1), 801 (1), 839 (2), 866(2), 919(2), 963(2), 997(2),1041(2), 1068 (2), 1081 (2), 1113 (1), 1149 (2), 1185 (2), 1215 (1), 1254 (8W), 1292 (8W), 1370 (3), 1415 (4), 1443 (7), 1451 (8), 1635 (10), 1654 (10W), 2854 (3), 2918 (8), 3015 (3), 3080 (3).

Bromine number by the McIlliney method, recomputed in terms of mols: 325, 320, 321. $C_8H_{14}F_2$. Calc. 320.

Lebedev hydrogenation. Adams platinic oxide [5] was employed as the catalyst. After the platinic oxide had been reduced, the hydrocarbon was placed in a "duck." The hydrogen consumption was read off every 0.5 minutes. The hydrocarbon weighed 0.6238 g.

Hydrogen consumption readings, ml (at 750.2 mm and 18.5°): 14; 13.1; 13.1; 13; 13; 12.9; 12.9; 12.6; 12.2; 11.4; 11; †† 8.8; 9.2; 9.9; 9.4; 9.1; 8.6; 8; 6.4; 6; 5.8; 4.8; 4.8; 3.8; 2.7; 2.6; 2.5; 2; 2; 2; 2; 1; 2; 1; 2.4; 2.2; 2.4; 2; 1.6; 1.4; 1; 1.2; 2.8; 0.6; 0.4; 0.6; 0.8; 0.1; 0.1; 0.1; 0.1:

The hydrogen consumption totaled 271 ml, or 250 ml at standard conditions. Calculations indicate that octadiene requires 254 ml. The symbol †† denotes the break in the hydrogenation curve. 139 ml of hydrogen, or 51.3%, were consumed up to the break.

13.7 g of the hydrocarbon were thoroughly hydrogenated to identify the hydrogenation product. After all the hydrogen had been added, the reaction mixture was poured into water, the hydrocarbon being separated, dried, and distilled. Its properties (b.p. 123-124°; $d_4^{20}$ 0.7190; $n_D^{20}$ 1.4034) were those of normal octane (b.p. 125.6°). The isomeric octanes boil within the 109-117° range.

Fraction with b.p. of 132-220°. Repeated fractionation yielded a hydrocarbon with a b.p. of 120-125° at 50 mm.

$d_4^{20}$ 0.8244; $n_D^{20}$ 1.45347; $\gamma^{20}$ 24.72 dynes/cm. Found: $MR_D$ 53.15; P 438; M 156 (cryoscopy in benzene). $C_{12}H_{18}F_3$. Calc. $MR_D$ 54.07;* P 435; M 162.

Bromine number, recomputed in mols: 450; calc. for three double bonds: 480.

## SUMMARY

1. Debromination of 1,4-dibromobutene-2 by metallic sodium in anhydrous ether splits off bromine, yielding 1,8-dibromoctadiene-2,6, which is then converted into octadiene-1,6, dodecatriene, and higher-molecular forms.

2. The reaction is an involved one. The high-polymer forms must exhibit increased unsaturation.

3. No cyclic hydrocarbons with four or eight carbon atoms are formed when bromine is split off from 1,4-dibromobutene-2, which agrees with the strain theory.

## LITERATURE CITED

[1] Ziegler, . Ann., 513, 43 (1934); Ber., 67, 140 (1934).

[2] S. V. Lebedev, G. G. Koblyansky, and A. I. Yakubchik, J. Russ. Chem. Soc. 56, 265 (1924).

[3] S. V. Lebedev and assoc., J. Russ. Chem. Soc. 56, 290 (1924).

[4] Thiele, .. Ann., 308, 333 (1899).

[5] Syntheses of organic preparations (Russ. ed.), Coll. 1, p. 357 (1949).

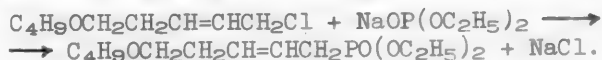*On the basis of $C_{12}H_{18}$ and four double bonds we get $MR_D$ (exper.) = 52.50; and $MR_D$ (calc.) = 53.55.

# ALLYL REARRANGEMENTS

## XV. REACTIONS BETWEEN THE SODIUM AND MAGNESIUM SALTS OF DIALKYL
## PHOSPHOROUS ACIDS AND ISOMERIC BUTOXYCHLOROPENTENES

### A. N. Pudovik

In one of our previous papers [1] we made a study of the reactions between
isomeric methoxychloropentenes and the sodium salts of dialkyl phosphorous acids.
It was shown that the reactions are normal, without rearrangement, when the primary
methoxychloropentene is employed, the reactions with secondary methoxychloro-
pentenes differing, depending upon whether free dialkyl phosphorous acids are
present in the reaction medium. When the acids are present alkoxy dialkyl phospho-
pentenes are formed, the structure of which is the same as that prepared from the
primary methoxychloropentene; when they are absent, products of further addition
of the sodium dialkyl phosphite being formed. Inasmuch as these reactions are of
considerable theoretical interest, we resolved to pursue their study, using other
compounds.

The present paper describes the reactions of the sodium and magnesium salts
of dialkyl phosphorous acids with isomeric butoxychloropentenes. The reaction of
1-butoxy-5-chloropentene-3 with sodium diethyl phosphite in an excess of diethyl-
phosphorous acid yielded 78.5% of 1-butoxy-5-diethylphosphopentene-3.

$$C_4H_9OCH_2CH_2CH=CHCH_2Cl + NaOP(OC_2H_5)_2 \longrightarrow$$
$$\longrightarrow C_4H_9OCH_2CH_2CH=CHCH_2PO(OC_2H_5)_2 + NaCl.$$

An analogous reaction with sodium dibutyl phosphite was unsuccessful, notwith-
standing a wide variation in the reaction conditions employed, a hyaline mass
that decomposed when heated in vacuo being produced in every instance. The reaction
of 1-butoxy-3-chloropentene-4 with sodium diethylphosphite in benzene, with
diethylphosphorous acid present, yielded 54% of 1-butoxy-5-diethylphosphopentene-3.
Similarly, the reaction with sodium dibutylphosphite yielded 49% of 1-butoxy-5-
dibutylphosphopentene-3.

Our experiments lead to the conclusion that the reactions of the Na salts
of dialkyl phosphorous acids with 1-butoxy-3-chloropentene-4, like those with 1-
methoxy-3-chloropentene-4, are monomolecular, involving a complete allyl
rearrangement. When there are no free acids in the reaction medium, the reactions
of 1-butoxy-3-chloropentene-4 with the sodium salts of dialkyl phosphorous acids
result in the formation of thick, tacky products that cannot be distilled in
vacuo.

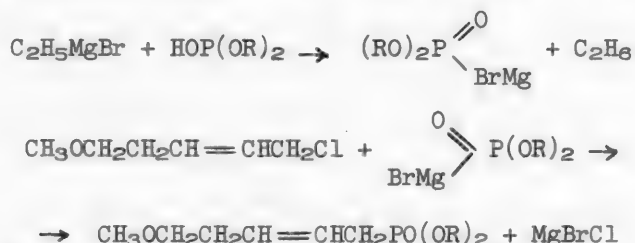Inasmuch as some of the reactions I carried out between salts of dialkyl

phosphorous acids and the isomeric butoxychloropentenes did not yield positive results, I endeavored to perform them with the corresponding magnesium salts. There are no definite statements in the literature regarding the feasibility of employing the magnesium salts of dialkyl phosphorous acids to synthesize phosphinic esters, so that a study of these reactions was of some theoretical interest.

The magnesium salts of the dialkyl phosphorous acids were initially prepared by adding a dialkyl phosphorous acid to an ether solution of ethylmagnesium bromide. We found that only about one third of the dialkyl phosphorous acid reacted, however, liberating ethane; adding the other two thirds of the acid had no effect. The reason for this peculiar trend of the reaction may be that the reaction of the diethylphosphorous acid with the Grignard reagent does not stop at the stage in which the magnesium salt of the diethylphosphorous acid is formed, but continues, yielding a salt of the dialkylphosphorous acid,

$$(C_2H_5O)_2P \overset{O}{\underset{MgBr}{<}} + 2C_2H_5MgBr \rightarrow (C_2H_5)_2P \overset{O}{\underset{MgBr}{<}} + 2C_2H_5OMgBr,$$
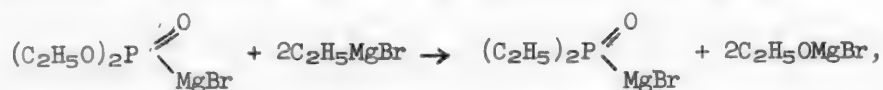
so that all the ethylmagesium bromide is rapidly removed from the reaction zone. Subsequently, the method used to prepare the magnesium salts of dialkyl phosphorous acids was modified so as add the Grignard reagent, prepared in ether, to a solution of the dialkyl phosphorous acid in benzene.

The action of magnesium diethylphosphite upon 1-methoxy-5-chloropentene-3 and 1-butoxy-5-chloropentene-3 yielded 1-methoxy-5-diethylphosphopentene-3 and 1-butoxy-5-diethylphosphopentene-3, the yields being 15.6 and 13.4%, respectively.

$$C_2H_5MgBr + HOP(OR)_2 \rightarrow (RO)_2P \overset{O}{\underset{BrMg}{<}} + C_2H_6$$

$$CH_3OCH_2CH_2CH = CHCH_2Cl + \underset{BrMg}{\overset{O}{>}} P(OR)_2 \rightarrow$$

$$\rightarrow CH_3OCH_2CH_2CH = CHCH_2PO(OR)_2 + MgBrCl$$

The reaction of the mixed magnesium salt of diethylphosphorous acid with 1-methoxy-3-chloropentene-4 yielded 1-methoxy-5-diethylphosphopentene-3, the yield being 18.4%. We did not manage to secure the expected products when we reacted 1-butoxy-3-chloropentene-4 with the magnesium salts of diethyl or dibutylphosphorous acids, further heating of the reaction mixtures, after the solvent had been driven off, converting them into solid hyaline polymers.

We may infer from these experiments that the magnesium salts of dialkyl phosphorous acids may be successfully employed in some cases to synthesize phosphine esters instead of salts of the alkali metals, though the product yields are considerably lower. As when sodium salts are used, the reactions with the magnesium salts of dialkyl phosphorous acids are bimolecular, with no rearrangement, when the primary allyl halogen isomers are used, and monomolecular, with a complete allyl rearrangement, when the secondary isomers are used.

### EXPERIMENTAL

Action of 1-butoxy-5-chloropentene-3 on sodium diethylphosphite. An ether solution of sodium diethylphosphite was prepared from 2 g of sodium and 12 g of diethylphosphorous acid, dissolved in 150 ml of absolute ether. 15 g of 1-butoxy-

5-chloropentene-3 was added gradually to the resultant solution, and then the mixture was heated on a water bath for 3 hours. A large quantity of sodium chloride was thrown down as soon as heating started. The sodium chloride was filtered out and washed repeatedly with ether, the ether being driven off and the residue distilled in vacuo. This yielded about 2 g of the original chloride, 1.5 g of a fraction that boiled in the 103-110° range (9 mm), and 19 g of 1-butoxy-5-diethylphosphopentene-3.

B.p. 169-171° (9 mm); $n_D^{20}$ 1.4462; $d_4^{20}$ 0.9918. 0.1384 g substance: 15.4 ml NaOH (T = 0.02085). Found %: P 10.84; $C_{13}H_{27}O_4P$. Calc. %: P 11.1.

Action of 1-butoxy-5-chloropentene-3 on dibutylphosphorous acid. 3.8 g of sodium was added to 28 g of dibutylphosphorous acid dissolved in 100 ml of anhydrous ether, and 26 g of 1-butoxy-5-chloropentene-3 was added after the sodium had dissolved. The reaction mass was heated on a water bath for 3 hours, the sodium chloride being filtered out and washed with ether. The ether was driven off, and the low-boiling fractions of the residue were distilled in vacuo. After it had been heated for a short time, it thickened into a transparent hyaline mass that decomposed when heated further.

Nor did repeated experiments, using a benzene solution and with an excess of dibutylphosphorous acid present, yield any positive results.

Action of 1-butoxy-3-chloropentene-4 on sodium diethylphosphite. 50 ml of absolute benzene and 30.7 g of 1-butoxy-3-chloropentene-4 were added to an ether solution of sodium diethylphosphite, prepared from 4 g of sodium and 48 g of diethylphosphorous acid. Sodium chloride began to precipitate out after the ether and part of the benzene had been driven off. The reaction mixture was heated on a water bath for 3 hours. The sodium chloride was filtered out and washed with ether. The ether and the benzene were driven off from the residue, the latter being fractionated in vacuo from a flask with a Widmer column. This yielded 5 g of the original chloride, 14 g of diethylphosphorous acid, and 26 g of 1-butoxy-5-diethylphosphopentene-3, whose constants were as follows: b.p. 169-171° (9 mm); $n_D^{20}$ 1.4461; $d_4^{20}$ 0.9918.

Action of 1-butoxy-3-chloropentene-4 on sodium dibutylphosphite. An ether solution of sodium dibutylphosphite was prepared from 40 g of dibutylphosphorous acid, 2.3 g of sodium, and 100 ml of anhydrous ether 35 ml of anhydrous benzene and 18 g of 1-butoxy-3-chloropentene-4 were gradually added to the foregoing solution of sodium dibutylphosphite. The ether was driven off, and the reaction mass heated on a water bath for 3 hours. The sodium chloride was filtered out, and the reaction mass fractionated, yielding 16.5 g of 1-butoxy-5-dibutylphosphopentene-3.

B.p. 190-191° (7 mm); $n_D^{20}$ 1.4478; $d_4^{20}$ 0.9685. 0.1420 g substance: 13.0 ml NaOH (T = 0.02085). 0.1536 g substance: 14.2 ml NaOH. Found %: P 8.94, 9.03. $C_{17}H_{35}O_4P$. Calc. %: P 9.28.

Action of 1-methoxy-5-chloropentene-3 on Magnesium diethylphosphite. An ether solution of ethylmagnesium bromide, prepared from 8 g of magnesium and 37 g of ethyl bromide, was slowly added, with vigorous stirring, to 46 g of diethylphosphorous acid. Ethane was liberated during this addition, and the reaction mass grew warm. 40 ml. of anhydrous benzene and 45 g of 1-methoxy-5-chloropentene-3 were added to the magnesium diethylphosphite thus prepared. The ether was then driven off, and the mixture heated on a water bath for 3 hours. The reaction products were treated with water and dilute hydrochloric acid and extracted several times with ether. The ether and the benzene were driven off, and the residue fractionated in vacuo. This yielded 15.6 g of the unreacted

1-methoxy-5-chloropentene-3, 4 g of diethylphosphorous acid, and 12.3 g of 1-methoxy-5-diethylphosphopentene-3 with the following constants: b.p. 150-152° (11 mm); $n_D^{20}$ 1.4471; $d_4^{20}$ 1.0382. The 1-methoxy-5-diethylphosphopentene-3 we had prepared by reacting sodium diethylphosphite with 1-methoxy-5-chlorpentene-3 had the following constants: b.p. 146-147° (8 mm); $n_D^{20}$ 1.4480; $d_4^{20}$ 1.0380.

Action of 1-butoxy-5-chloropentene-3 on magnesium diethylphosphite. A Grignard reagent prepared from 2 g of magnesium, 9 g of ethyl bromide, and 150 ml of absolute ether, was gradually added to 11 g of diethylphosphorous acid. Then 35 ml of absolute benzene and 15 g of 1-butoxy-5-chloropentene-3 were added to the resultant magnesium salt. The ether and part of the benzene were driven off, and the reaction mixture was heated on a water bath for 3 hours. Processing and fractionation of the reaction mixture yielded 2 g of the original chloride, 3 g of diethylphosphorous acid, and 3.1 g of 1-butoxy-5-diethylphospho-pentene-3 with the following constants: b.p. 169° (9 mm); $n_D^{20}$ 1.4462; $d_4^{20}$ 0.9916. The residue in the flask consisted of a tacky yellow nondistillable mass.

Action of 1-methoxy-3-chloropentene-4 on magnesium diethylphosphite. A Grignard reagent, prepared from 2 g of magnesium, 9 g of ethyl bromide, and 100 ml of absolute alcohol, was added to 11 g of diethylphosphorous acid. Then 40 ml of absolute benzene and 12 g of 1-methoxy-3-chloropentene-4 were added to the reaction mixture. The ether and part of the benzene were driven off, and the residue was heated on a water bath for 3 hours. Processing and fractionation of the reaction mixture yielded 7 g of a fraction that distilled up to 50° at 14 mm, 4 g of a fraction that distilled at 50-76° (11 mm), and 3.5 g of 1-methoxy-5-diethylphosphopentene-3 with the following constants: B.p. 150-152° (11 mm); $n_D^{20}$ 1.4442; $d_4^{20}$ 1.0383. The residue left in the flask was a solid, hyaline type of resin. Refractionation of the first two fractions yielded 4.5 g of the original chloride and 3 g of a fraction that distilled at 58-69° (10 mm).

Action of 1-butoxy-3-chloropentene-4 on magnesium dibutylphosphite. The reaction resembled the one described in the foregoing test, the Grignard reagent being prepared from 3 g of magnesium, 14 g of ethyl bromide, and 150 ml of absolute ether. It was added to a solution of dibutylphosphorous acid, after which 45 ml of benzene and 22 g of 1-butoxy-3-choropentene-4 were poured into the reaction mixture. Processing and fractionation of the reaction mixture yielded 5 g of the original chloride and 7 g of a fraction that distilled at 65-70° (10 mm); the residue consisted of 13 g of a transparent yellow resin.

Tests to determine the amount of ethane evolved in the reaction of ethyl-magnesium bromide with diethylphosphorous acid. A Grignard reagent with a total volume of 200 ml was prepared from 10 g of magnesium, 48 g of ethyl bromide, and 150 ml of absolute ether. According to the equation:

$$(C_2H_5O)_2POH + C_2H_5MgBr \rightarrow (C_2H_5O)_2P{\overset{O}{\underset{MgBr}{\diagup}}} + C_2H_6$$
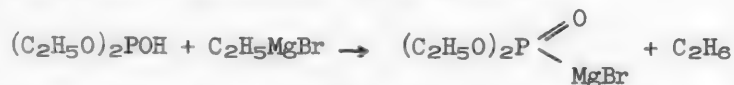
1.4 g of diethylphosphorous acid should have been consumed for 5 ml of the Grignard reagent containing 0.24 g of Mg, and 225 ml of ethane should have been evolved.

The tests were run as follows: the diethylphosphorous acid was added a drop at a time to a measured volume of the Grignard reagent, the ethane given off being measured in a buret. The results are listed in the table.

| Test No. | Ml of Grignard reagent | Grams of diethylphosphorus acid | | Ml of ethane | |
|---|---|---|---|---|---|
| | | Theoretical | Actual | Theoretical | Actual |
| 1 | 5 | 1.4 | 0.46 | 225 | 73 |
| 2 | 10 | 2.8 | 0.70 | 450 | 113 |
| 3 | 20 | 5.6 | 1.8 | 900 | 295 |

## SUMMARY

1.  A study has been made of the action of sodium and magnesium salts upon the isomeric butoxy- and methoxychloropentenes.

2.  It has been shown that the magnesium salts of dialkyl phosphorous acids may be employed to synthesize phosphinic esters.

3.  The reactions of sodium and magnesium salts of dialkyl phosphorous acids with primary butoxychloropentene are normal, no rearrangement being involved; Their reactions with the secondary butoxychloropentenes, on the other hand, involve a complete allyl rearrangement, yielding alkoxy dialkyl phosphopentenes whose structure is the same as those prepared from the primary chlorides.

## LITERATURE CITED

[1]  A. N. Pudovik and B. A. Arbuzov, Bull. USSR Acad. Sci. Div. Chem. Sci. 1949, No.5, 522.

Laboratory of Organic Chemistry,
The V. I. Ulyanov-Lenin State University of Kazan.

# RESEARCH ON TERTIARY ALCOHOLS CONTAINING A CYCLOBUTYL RADICAL
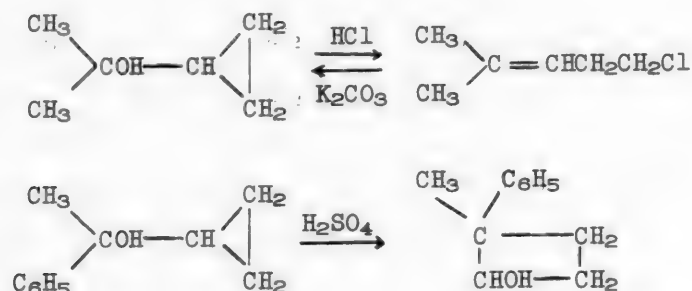
## I. THE REACTION OF DIISOPROPYLCYCLOBUTYLCARBINOL WITH HYDROCHLORIC

## AND SULFURIC ACIDS

T. A. Favorskaya and I. P. Yakovlev

Research on the polymethylene hydrocarbons and their derivatives is largely the work of Russion scientists. The basic research on the chemistry of the derivatives of cyclopropane and cyclobutane has been done chiefly by N. Ya. Demyanov and N. M. Kizhner, who established that these cyclic systems were not very stable and converted them into compounds with open chains of carbon atoms or into more stable compounds. N. M. Kizhner [1], for example, showed that the reaction of hydrobromic and hydriodic acids upon dimethylcyclobutylcarbinol, diethylcyclobutylcarbinol, and diphenylcyclobutylcarbinol involved the expansion of the four-membered ring to a five-membered one. N. Ya. Demyanov [2] was the first to show that the action of concentrated HBr on cyclopropylcarbinol resulted in the formation of isomerization products – bromocyclobutane and 2-bromobutene-3 – in addition to the normal reaction product – cyclopropylbromomethane [3]. The same two isomeric bromides are formed when hydrobromic acid reacts with cyclobutanol [4]. Concentrated HBr and HI isomerize cyclobutylcarbinol to bromine and iodine derivatives of cyclopentane, while ethylcyclobutylcarbinol is isomerized and its ring is expanded when acted upon by these acids [5]. B. A. Kazansky [6] tried to dehydrate dimethylcyclobutylcarbinol with metallic sodium in decalin at 120°, without acids present. The reaction followed two lines, the cyclobutane ring being preserved. When reacted with HBr, diphenylcyclopropylcarbinol yields a bromide, to which Lipp [7] attributed the structure of diphenylcyclopropylbromomethane. Since the bromide was highly inert, N. M. Kizhner was forced to assume that the author had actually secured 1,1-diphenyl-2-bromocyclobutane, whereupon he reacted diphenylcyclobutylcarbinol with hydrobromic acid, again securing a highly inert bromide [8]. This led the author to assert that here, as in the derivatives of triphenylcarbinol, the bromine may be shifted to the phenyl radical. Apparently here, as in the bromide of diphenylcyclopropylcarbinol, the ring was enlarged, yielding 1,1-diphenyl-2-bromocyclopentane, which could explain the high inertness of the synthesized bromide.

T. A. Favorskaya has recently investigated the reaction of hydrochloric and sulfuric acids with tertiary cyclopropane alcohols: dimethylcyclopropylcarbinol [9], methylethylcyclopropylcarbinol [10], and methylphenylcyclopropylcarbinol [11]. Hydrochloric acid converts the first two of these alcohols into unsaturated
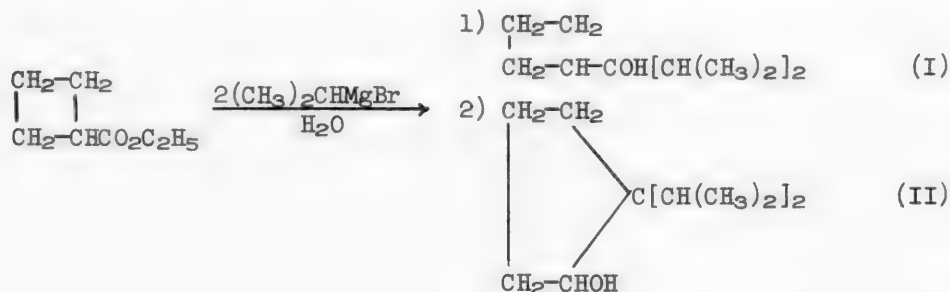
derivatives and opens the carbon ring, whereas this is supplemented by the
formation of derivatives of cyclobutane in the case of methylphenylcyclopropyl-
carbinol.

$$\begin{array}{c}CH_3\\CH_3\end{array}\!\!>\!\!COH\!\!-\!\!CH\!\!<\!\!\begin{array}{c}CH_2\\|\\CH_2\end{array}\quad\underset{K_2CO_3}{\overset{HCl}{\rightleftharpoons}}\quad\begin{array}{c}CH_3\\CH_3\end{array}\!\!>\!\!C=CHCH_2CH_2Cl$$

$$\begin{array}{c}CH_3\\C_6H_5\end{array}\!\!>\!\!COH\!\!-\!\!CH\!\!<\!\!\begin{array}{c}CH_2\\|\\CH_2\end{array}\quad\xrightarrow{H_2SO_4}\quad\begin{array}{cc}CH_3\;\;\;C_6H_5\\\;\;\diagdown\;\;\diagup\\C\!\!-\!\!-\!\!-\!\!CH_2\\|\qquad\quad|\\CHOH\!\!-\!\!CH_2\end{array}$$

When the chlorides prepared from dimethylcyclopropylcarbinol and methylethyl-
cyclopropylcarbinol were heated with a potash solution, they were converted
into the initial cyclic alcohols.  When unsaturated chlorides prepared from
methylphenylcyclopropylcarbinol were heated with an aqueous solution of an
alkali, they were converted into diethylenic hydrocarbons;  under these same
conditions the cyclic chloride proved to be extraordinarily stable, being re-
covered unchanged even after 150 hours of heating.  Only after the chloride
had been treated with an alcoholic solution of NaOH was hydrogen chloride split
off and the four-membered ring ruptured, yielding a diethylenic hydrocarbon.

The diversity of the transformations observed in the papers cited and
the little research that has been done on tertiary alcohols that contain a
cyclobutyl radical led us to undertake a study of the reaction of several
alcohols of this type with hydrochloric and sulfuric acids.

We synthesized diisopropylcyclobutylcarbinol from the ethyl ester of
cyclobutanecarboxylic acid and isopropylmagnesium bromide in a Grignard re-
action.  We observed the first recorded instance of the simultaneous forma-
tion of two isomeric cyclic alcohols, viz.:  diisopropylcyclobutylcarbinol and
1,1-diisopropylcyclopentanol-2, in an organomagnesium synthesis of compounds
containing a cyclic radical.  The alcohol yield was practically independent
of the reaction conditions, about 70% of diisopropylcyclobutylcarbinol and
about 30% of 1,1-diisopropylcyclopentanol-2, based on the total alcohols syn-
thesized, being formed in every case.  Moreover, a minute quantity of an un-
saturated product, which we managed to process with a $KMnO_4$ solution, was al-
ways found in the alcohols.

$$\begin{array}{c}CH_2\!\!-\!\!CH_2\\|\qquad\quad|\\CH_2\!\!-\!\!CHCO_2C_2H_5\end{array}\quad\xrightarrow[H_2O]{2(CH_3)_2CHMgBr}$$

1) $\begin{array}{c}CH_2\!\!-\!\!CH_2\\|\\CH_2\!\!-\!\!CH\!\!-\!\!COH[CH(CH_3)_2]_2\end{array}$     (I)

2) $\begin{array}{c}CH_2\!\!-\!\!CH_2\\|\qquad\qquad\diagdown\\\qquad\qquad\quad C[CH(CH_3)_2]_2\\|\qquad\qquad\diagup\\CH_2\!\!-\!\!CHOH\end{array}$     (II)
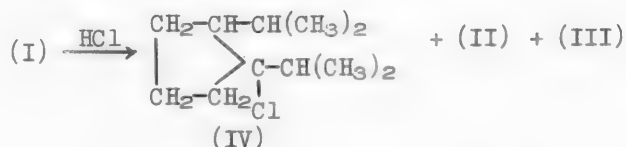
The oxidation products of the unsaturated compound found in the alcohols yielded formic and oxalic acids. It is difficult to form an idea of the structure of the unsaturated compound from the formation of these two acids. The syntheses of dimethyl-, diethyl-, and diphenylcyclobutylcarbinols apparently do not result in the formation of isomeric alcohols and unsaturated products, since there are no references thereto in the literature. The organomagnesium complex was carefully decomposed with pieces of ice, and the ether layer that separated was decanted, the isomerization of the previously prepared diisopropylcyclobutylcarbinol into 1,1-diisopropylcyclopentanol-2 occurring only when the action of the acids upon the initial alcohol is fairly energetic. It must therefore be admitted that the isomeric alcohol was formed by the isomerization of the organomagnesium complex at the instant of its formation.

The structure of the synthesized alcohols was established by oxidizing them with a chromic acid mixture. Oxidation of diisopropylcyclobutylcarbinol yielded cyclobutanecarboxylic acid; in one run diisopropylcyclopentanol-2 yielded the hydroxy acid $HO_2CCH_2CH_2CH_2C(OH)[CH(CH_3)_2]_2$, which was isolated as the lactone with a b.p. of 80-83°, and in another $\alpha,\alpha$-diisopropylglutaric acid $HO_2CCH_2CH_2C$-$-(CO_2H)[CH(CH_3)_2]_2$ with a m.p. of 168-170° being produced. The hydroxycarboxylic acid was produced when the chromic acid mixture was poured into the alcohol, the dicarboxylic acid being produced when the alcohol was poured into the chromic acid. The former resulted from rupture of the ring at the 1,2 position, the latter from ring rupture at the 2,3 position.

Heating diisopropylcyclobutylcarbinol to 100° for 6 hours with 25% sulfuric acid yielded no isomerization product, though partial isomerization to diisopropylcyclopentanol-2 took place when 50% sulfuric acid was employed. The principal reaction product was the unsaturated hydrocarbon diisopropylmethylenecyclobutane (25-30% of the initial alcohol by weight). The reaction involved considerable tarring.
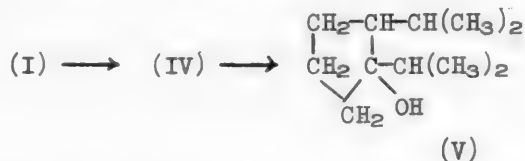
$$(I) \longrightarrow \begin{matrix} CH_2-CH_2 \\ | \quad\quad | \\ CH_2-C=C[CH(CH_3)_2]_2 \end{matrix} + (II)$$
$$(III)$$
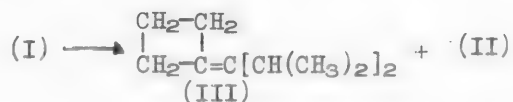
Diisopropcyclcyclobutylcarbinol did not react with 18% hydrochloric acid, but when an excess of a 36% acid was used, the chloride (IV) was the principal reaction product, plus an unsaturated hydrocarbon that was identical with the hydrocarbon secured in the reaction of diisopropylcyclobutylcarbinol with sulfuric acid, and an isomeric alcohol, diisopropylcyclopentanol-2, which was identical with the alcohol produced in the organomagnesium synthesis and in the reaction with sulfuric acid.

$$(I) \xrightarrow{HCl} \begin{matrix} CH_2-CH-CH(CH_3)_2 \\ | \quad\quad\quad\rangle C-CH(CH_3)_2 \\ CH_2-CH_2\;\;| \\ \quad\quad\quad Cl \end{matrix} + (II) + (III)$$
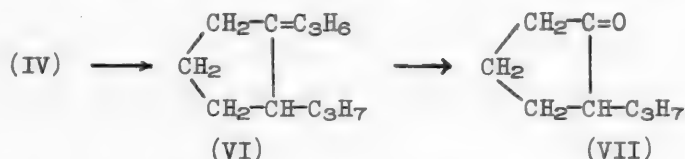$$(IV)$$

Reacting 1,1-diisopropylcyclopentanol-2 with 36% HCl under the same conditions as those used for diisopropylcyclobutylcarbinol yielded the chloride (VIII), b.p. 66-67° (19 mm), and the chloride (IX), b.p. 110° (18 mm).
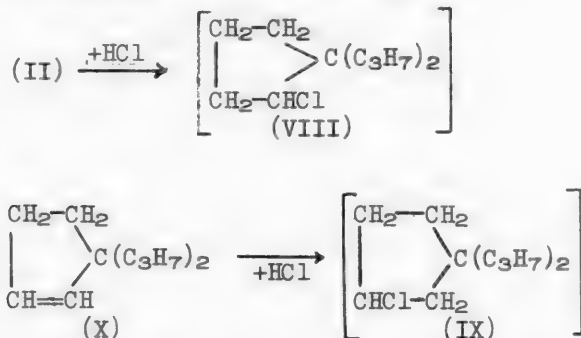
The percentage of chlorine, determined by the Carius method, was the same in all the three chlorides, being equivalent to one atom of chlorine per molecule of the compound. Efforts to saponify the chlorides (VIII) and (IX) with potash met with failure. The chloride (IV), on the other hand, was saponified readily, yielding the alcohol 1,2-diisopropylcyclopentanol-1. The chloride (IV) is a five-membered cyclic compound, produced by the isomerization of the four-membered ring to a five-membered one and the shift of one isopropyl group from the 1,1 position to the 1,2 position:

$$(I) \longrightarrow (IV) \longrightarrow
\begin{array}{l}
CH_2-CH-CH(CH_3)_2 \\
\quad | \qquad | \\
CH_2 \;\; C-CH(CH_3)_2 \\
\quad \diagdown \quad | \\
\qquad CH_2 \;\; OH
\end{array}$$
$$(V)$$

As a matter of fact, splitting elements of hydrogen chloride from this chloride with sodium ethylate yielded an unsaturated hydrocarbon that differed appreciably from the other hydrocarbons synthesized. In view of the danger of having a trace of other unsaturated hydrocarbons, it was not distilled with sodium although it contained traces of the chloride (Beilstein test). Ozonization of the hydrocarbon yielded isopropylcyclopentanone, the semicarbazone of which had a m.p. of 119°. The reaction was as follows:

$$(IV) \longrightarrow
\begin{array}{l}
\quad\; CH_2-C=C_3H_6 \\
CH_2 \qquad\quad | \\
\quad\; CH_2-CH-C_3H_7
\end{array}
\longrightarrow
\begin{array}{l}
\quad\; CH_2-C=O \\
CH_2 \qquad\quad | \\
\quad\; CH_2-CH-C_3H_7
\end{array}$$
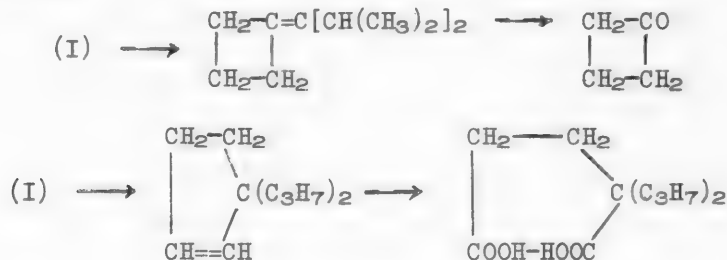$$\qquad\qquad\qquad (VI) \qquad\qquad\qquad\qquad (VII)$$

The formation of two chlorides from diisopropylcyclopentanol is explainable on the assumption that the reaction followed three lines: 1) formation of the normal product of the substitution of chlorine for the hydroxyl group; 2) formation of an unsaturated hydrocarbon; and 3) addition of HCl at the instant the unsaturated hydrocarbon is formed, when the molecule is in an activated state, the chlorine entering at the 3 position, viz.:

$$(II) \xrightarrow{\;+HCl\;}
\left[
\begin{array}{l}
CH_2-CH_2 \\
| \qquad\qquad \diagup C(C_3H_7)_2 \\
CH_2-CHCl \\
\quad\;\; (VIII)
\end{array}
\right]$$

$$
\begin{array}{l}
CH_2-CH_2 \\
| \qquad\quad \diagdown C(C_3H_7)_2 \\
CH=CH \\
\quad (X)
\end{array}
\xrightarrow{\;+HCl\;}
\left[
\begin{array}{l}
CH_2-CH_2 \\
| \qquad\qquad \diagdown C(C_3H_7)_2 \\
CHCl-CH_2 \\
\quad\;\; (IX)
\end{array}
\right]$$

No precise determination of the position of chlorine in the chlorides (VIII) and (IX) was made, owing to the small quantities at our disposal.

When reacted with 50% sulfuric acid 1,1-diisopropylcyclopentanol yielded
an unsaturated hydrocarbon with a b.p. of 74-75° at 20 mm. The hydrocarbon
secured from diisopropylcyclobutylcarbinol had a b.p. of 39-42° at 19 mm.
Hence, different unsaturated hydrocarbons were secured in these two cases.
The structure of the synthesized hydrocarbons was established by ozonization,
cyclobutanone being produced from the first one, and $\alpha,\alpha$-diisopropylglutaric
acid from the second.

$$(I) \longrightarrow \begin{array}{c} CH_2\text{-}C\text{=}C[CH(CH_3)_2]_2 \\ | \quad\quad | \\ CH_2\text{-}CH_2 \end{array} \longrightarrow \begin{array}{c} CH_2\text{-}CO \\ | \quad\quad | \\ CH_2\text{-}CH_2 \end{array}$$

$$(I) \longrightarrow \begin{array}{c} CH_2\text{-}CH_2 \\ | \quad\quad \backslash \\ \quad\quad C(C_3H_7)_2 \\ | \quad\quad / \\ CH\text{==}CH \end{array} \longrightarrow \begin{array}{c} CH_2\text{----}CH_2 \\ | \quad\quad\quad \backslash \\ \quad\quad\quad C(C_3H_7)_2 \\ | \quad\quad\quad / \\ COOH\text{-}HOOC \end{array}$$

## EXPERIMENTAL

The initial substances used in the synthesis of diisopropylcyclobutylcar-
binol were the ethyl ester of cyclobutanecarboxylic acid: $n_D^{21}$ 1.4234; $d_4^{21.5}$
0.9538; b.p. 157-161° (prepared from cyclobutanecarboxylic acid), and isopropyl
bromide. All our efforts to secure a high yield of the diisopropylcyclobutyl-
carbinol met with failure. We always obtained a mixture of two alcohols, 70%
of the total being diisopropylcyclobutylcarbinol, and 30% being the five-membered
cyclic alcohol 1,1-diisopropylcyclopentanol-2. The best conditions for synthes-
izing diisopropylcyclobutylcarbinol were as follows.

1 mol of isopropyl bromide in 200 ml of ether was added a drop at a time to
1 mol of magnesium shavings in the vessel ordinarily used for organomagnesium
synthesis, fitted with a stirrer and well-chilled, after which a solution of
0.5 mol of the ethyl ester of cyclobutanecarboxylic acid in 60 ml of ether was
added. When all the ether had been added, the reaction mixture was heated on
a water bath to a gentle boil for an hour, after which it was cooled with water,
and the organomagnesium complex was decomposed with pieces of ice. The ether
layer was decanted, and the basic magnesium bromide decomposed with dilute (1:5)
hydrochloric acid and extracted with ether, the ether extract being washed once
each with a soda solution and with water and then combined with the bulk of the
ether and dried over $Na_2SO_4$. The ether was then driven off, and the resultant
product fractionated into a column (at 9.5 mm), two alcohols being isolated:
18 g of one with a b.p. of 60-62°, and 5 g of another with a b.p. of 84-88°.
The residue totaled 6 g of tar, while 23 g of the ethyl ester of cyclobutane-
carboxylic acid was recovered unchanged. The alcohols contained an unsat-
urated impurity, which was eliminated by treatment with a 1% $KMnO_4$ solution.

One alcohol, diisopropylcyclobutylcarbinol, was a mobile liquid with a
barely perceptible yellowish tinge and the typical odor of tertiary alcohols.
It did not react with phthalic anhydride.

B.p. 60-61° at 9.5 mm, 161-165° at 756 mm; $n_D^{18.5}$ 1.4495; $\omega_{FCD}$ 21.2, $d_4^0$
0.9125; $d_4^{22.4}$ 0.8915; $MR_D$ 51.66; Calculated 52.32.

0.1054 g substance: 0.2970 g $CO_2$; 0.1315 g $H_2O$. 0.1310 g substance:
0.3682 g $CO_2$; 0.1620 g $H_2O$. Found %: C 76.85, 76.65; H 13.86, 13.74.

0.0503 g substance; 20.70 g benzene· $\Delta$t 0.071°. Found: $\underline{M}$ 171.3.
$C_{11}H_{22}O$. Calculated %: C 76.87; H 13.81. $\underline{M}$ 171.5.

The other alcohol, 1,1-diisopropylcyclopentanol-2, was a less highly mobile liquid with a faint peppermint odor. It reacted with phthalic anhydride to form a derivative with a m.p. of 185°.

B. p. 83-86° at 9.5 mm; $n_D^{21.3}$ 1.4591; $\omega_{FCD}$ 19.6; $d_4^0$ 0.9276; $d_4^{21.3}$ 0.9098; $MR_D$ 51.15; Calculated 52.32.

0.1777 g substance· 0.4991 g $CO_2$; 0.2201 g $H_2O$. Found %: C 76.83; H 13.86. 0.0412 g substance; 18.08 g benzene: $\Delta$t 0.064°. Found %: $\underline{M}$ 171.0. $C_{11}H_{22}O$. Calculated %: C 76.87; H 13.81. $\underline{M}$ 171.5.

Both alcohols reacted with metallic sodium, giving off hydrogen. A test for the presence of a carbonyl group was negative

Oxidation of the alcohol with a b.p. of 83-86° at 9.5 mm. 4 g of the alcohol was placed in a round-bottomed flask fitted with a stirrer, and a mixture of 19.4 g of potassium bichromate, dissolved in 24.5 g of $H_2SO_4$ (1.84), and 80 ml of water was added drop by drop at room temperature. After two hours of oxidation, the temperature was raised to 80°. Then the mixture was heated to 90° for another 3 hours. After the reaction mixture had cooled and been diluted with 100 ml of water, the reaction product was extracted with benzene and dried over $Na_2SO_4$, the 2.3 g of the resulting product being fractionated in vacuo. This yielded a fraction with a b.p. of 80-83° at 9 mm, which did not react with phenylhydrazine, but slowly dissolved in alkali. The neutralization equivalent was determined by back-titration.

0.1561 g substance: 19.0 ml NaOH; 7.9 ml HCl ($T_{NaOH}$ 0.003505; $T_{HCl}$ 0.004223). Found: equiv. 206.9. $C_{11}H_{22}O_3$. Calculated: equiv. 202.7.

These findings are evidence of the formation of a hydroxy acid; oxidation of 1,1-diisopropylcyclopentanol-2 could yield the hydroxy acid $\delta$, $\delta'$-diisopropyl- -$\delta$-hydroxyvaleric acid. When the alcohol was added to the chromic acid mixture, a dicarboxylic acid with a m.p. of 168-170° was produced instead of the hydroxy acid.

0.0920 g substance: 10 ml NaOH; 0.2 ml $H_2SO_4$. 0.1098 g substance: 14.0 ml NaOH; 1.4 ml $H_2SO_4$ ($T_{NaOH}$ 0.003505; $T_{H_2SO_4}$ 0.005428). Found: equiv. 108.5, 106.5. $C_{11}H_{20}O_4$. Calculated: equiv. 108.8. 0.0671 g substance: 0.0332 g Ag. 0.1551 g substance: 0.0768 g Ag. Found %: Ag 49.60, 49.70. $C_{11}H_{18}O_4Ag_2$. Calculated %: Ag 50.02.

The analysis of the silver salt and the neutralization equivalent of this acid indicate that it is 2,2-diisopropylglutaric acid, which could result from rupture of the five-membered ring between the CHOH and $CH_2$ groups. The structure of this acid was not confirmed by synthesizing it. The silver salt of $\alpha,\alpha$-diisopropylglutaric acid is fairly freely soluble in water.

Oxidation of the alcohol with a b.p. of 60-61° at 9.5 mm. In this oxidation we used 4 g of the alcohol, 19.4 g of potassium bichromate, 40 ml of water, and 24.5 g of sulfuric acid (sp. gr. 1.84), the alcohol being added to a hot solution of the oxidizing mixture. Heat was evolved in the reaction, so that the flask had to be chilled. After all the alcohol had been added, the mixture was heated to 55-60° until the alcohol odor had disappeared, after which it was cooled, diluted with 150 ml of water, extracted with ether, dried over $Na_2SO_4$, and fractionated.

This yielded cyclobutanecarboxylic acid with a b.p. of 95° at 16 mm, which agrees with the figure given in the literature (95° at 15 mm).

Found: $\underline{M}$ 110.0. $C_5H_8O_2$. Calculated: $\underline{M}$ 100.0. Found %: Ag 51.70, 51.00. $C_5H_7O_2Ag$. Calculated: Ag 51.8.

Reaction of diisopropylcyclobutylcarbinol with sulfuric acid. Preliminary experiments with 25% sulfuric acid showed that the alcohol was not isomerized.* Nor did 50% produce isomerization at 50°, all the alcohol being recovered unchanged. But when the temperature of the reaction mixture was raised to 100°, the alcohol did react, 18 g of the alcohol yielding 1.5 g of an unsaturated hydrocarbon with a b.p. of 42-46° at 24 mm, 1.5 g of 1,1-diisopropylcyclopentanol-2 with a b.p. of 84° at 9 mm, 4 g of tar, and 6 g of the initial alcohol. The contact time was 6 hours in all the runs.

The unsaturated hydrocarbon, diisopropylmethylenecyclobutane, was a highly mobile liquid that smelled like kerosene. After the hydrocarbon had been distilled with sodium, it had a b.p. of 128-129° at 757 mm.

$n_D^{21.8}$ 1.4487; $\omega_{FCD}$ 24.2; $d_4^0$ 0.8119; $d_4^{21.8}$ 0.7950; $MR_D$ 51.79; Calculated: 50.33.

0.0501 g substance: 0.1596 g $CO_2$; 0.0613 g $H_2O$. 0.0533 g substance: 0.1701 g $CO_2$; 0.0621 g $H_2O$. Found %: C 86.93, 87.15; H 13.53, 12.74. 0.0163 g substance; 16.58 g benzene: $\Delta t$ 0.032°. 0.0477 g substance; 16.58 g benzene: $\Delta t$ 0.093°. Found: $\underline{M}$ 156.3, 160.5. $C_{11}H_{20}$. Calculated %: C 86.84, H 13.15. $\underline{M}$ 153.5.

After the isomeric alcohol 1,1-diisopropylcyclopentanol-2 had been carefully fractionated, it had a sharp boiling point of 120° at 19 mm (0.95 g); $n_D^{21}$1.4580; $\omega_{FCD}$ 19.8; $d_4^{21}$ 0.9100; $MR_D$ 51.0; Calculated 52.32. The constants of the isomeric alcohol were the same as those of the 1,1-diisopropylcyclopentanol produced during the synthesis of diisopropylcyclobutylcarbinol.

Reaction of diisopropylcyclobutylcarbinol with hydrochloric acid. The alcohol did not react with 18% hydrochloric acid at 100°. When reacted with 36% hydrochloric acid at room temperature for 36 hours, the alcohol yielded an unsaturated hydrocarbon, the chloride (IV), and an alcohol. The constants of the unsaturated hydrocarbon and of the alcohol corresponded with those of the diisopropylmethylenecyclobutane and the 1,1-diisopropylcyclopentanol-2, respectively, synthesized in the reaction of the alcohol with sulfuric acid.

0.0303 g substance; 16.55 g benzene: $\Delta t$ 0.062°. 0.0753 g substance; 16.55 g benzene: $\Delta t$ 0.153°. Found: $\underline{M}$ 148.7, 149.5. $C_{11}H_{20}$. Cal-$\underline{M}$ 153.5.

The chloride (IV) was a barely yellowish, mobile liquid.

B.p. 64.66° at 17 mm; $n_D^{19.4}$ 1.4511; $\omega_{FCD}$ 19.5; $d_4^{19.4}$ 0.9037; $MR_D$ 55.34; Calculated. 55.48.

---

*The solutions of hydrochloric and sulfuric acids were prepared from a mixture of equal parts of water and ethyl alcohol, and the corresponding weight of the concentrated acid (sp. gr. 1.84 for the sulfuric and 1.19 for the hydrochloric acid).

0.3162 g substance: 0.2320 g AgCl. 0.3524 g substance: 0.2616 g AgCl. Found %: Cl 18.15, 18.36. $C_{11}H_{21}Cl$. Calculated %: Cl 18.64.

Saponification of the chloride (IV). 3.4 g of the chloride was heated to boiling with 40 ml of a 10% potash solution for 20 hours. Processesing of the saponification product and vacuum fractionation yielded 0.5 g of an alcohol with a b.p. of 105-108° at 17 mm; $n_D^{19.5}$ 1.4567; $\omega_{FCD}$ 18.8. The synthesized alcohol did not react with phthalic anhydride. The structure of the synthesized alcohol was not established nor was it analyzed, owing to the small quantity obtained. But in view of the fact that the chloride (IV) yielded the unsaturated hydrocarbon (VI) and that the latter yielded the ketone (VII), it must be assumed that the alcohol synthesized by saponification was a tertiary, five-membered alcohol. This is supported by the boiling point and the $n_D$ and $\omega_{FCD}$. Its tertiary nature is indicated by its inertness toward phthalic anhydride. A secondary alcohol reacted with phthalic anhydride, as we have seen.

Reaction of 1,1-diisopropylcyclopentanol-2 with 36% hydrochloric acid. 60 ml of 36% hydrochloric acid was added to 12 g of the alcohol, and the mixture was allowed to stand at room temperature for two days. Then the mixture was poured into 150 ml of water. The reaction product was extracted with ether, dried over $Na_2SO_4$, and fractionated in vacuo. The two chlorides (VIII) and (IX) were isolated.

The chloride (VIII) was a highly mobile liquid with a rather fragrant odor.

B.p. 66-67° at 19 mm; $n_D^{19.4}$ 1.4575; $\omega_{FCD}$ 19.7; $d_4^0$ 0.8954; $d_4^{19.4}$ 0.8815; $MR_D$ 58.33; Calculated 55.48.

0.2430 g substance: 0.1802 g AgCl. 0.3215 g substance: 0.2382 g AgCl. Found %: Cl 18.30, 18.33. $C_{11}H_{21}Cl$. Calculated %: Cl 18.64.

The chloride (IX) was a slightly mobile yellowish liquid with an unpleasant odor.

B.p. 110° at 18 mm; $n_D^{19.5}$ 1.4767; $\omega_{FCD}$ 19.6; $d_4^0$ 0.9775; $d_4^{19.5}$ 0.9642; $MR_D$ 55.65; Calculated 55.48.

0.2747 g substance: 0.3026 g AgCl. 0.2060 g substance: 0.2180 g AgCl. Found %: Cl 18.34, 17.87. $C_{11}H_{21}Cl$. Calculated %: Cl 18.64.

Saponification of the chlorides (VIII) and (IX). Saponification was conducted for 48 hours with a 20% potash solution at the boiling points of the solutions, but we were unable to saponify the chlorides. The physical constants of the reaction products were the same as those of the initial chlorides.

Reaction of 1,1-diisopropylcyclopentanol-2 with sulfuric acid. 5 g of the alcohol was heated to 80-85° for 12 hours with 10 ml of 50% $H_2SO_4$. Then the mixture was diluted with 50 ml of water. The reaction product was extracted with ether, dried over $Na_2SO_4$, and fractionated, yielding an unsaturated hydrocarbon.

B p. 74-75° at 20 mm; $n_D^{19.5}$ 1.4562; $\omega_{FCD}$ 23.1; $d_4^0$ 0.8390; $d_4^{19.5}$ 0.8243; $MR_D$ 50.64; Calculated 50.33. 0.0712 g substance: 0.2277 g $CO_2$; 0.0869 g $H_2O$. Found %: C 87.27; H 13.35. 0.0151 g substance; 16.5 g benzene: $\Delta t$ 0.031°. 0.0127 g substance; 16.5 g benzene: $\Delta t$ 0.029°. Found: $\underline{M}$ 151.5, 159.5. $C_{11}H_{20}$. Calculated %: C 86.84; H 13.15. $\underline{M}$ 156.1.

Ozonolysis of the unsaturated hydrocarbons. 1.2 g of the unsatured hydrocarbon secured from diisopropylcyclobutylcarbinol and 1.3 g of the hydrocarbon secured from 1,1-diisopropylcyclopentanol-2 were ozonized, the 2.5 g of hydrocarbons requiring 0.77 g of ozone. The ozone was passed through at 0.00535 g

per minute. After 2.5 hours had elapsed the percentage of ozone was practically identical at the inlet and outlet ends of the apparatus, which indicated that the reaction was complete. The chloroform was removed from the ozonization product by means of a capillary in vacuo. The ozonization product was decomposed with water, yielding cyclobutanone with a b.p. of 90-110° (the literature gives the b.p. of cyclobutanone as 100° at 760 mm) and $\alpha,\alpha$-diisopropylglutaric acid, which we did not manage to crystallize, although its consistency was very thick. We also secured a minute amount of a substance with a b.p. of 130-145°, the nature of which we were unable to determine. This must be diisopropyl ketone (b.p. 124.5°) with a minute trace of hydrocarbons that prevented the isolation of the semicarbazone in the crystalline state.

The semicarbazone of the cyclobutanone melted at 195-202° with decomposition, which agrees with the figure given in the literature.

Found %: N.33.88. $C_5H_9ON_3$. Calc. %: 33.05. 0.3316 g substance: 34.4 ml NaOH (T 0.003515). 0.1882 g substance: 20.0 ml NaOH; 0.8 ml HCl (T 0.004197). Found: equiv. 116.0, 106.8. $C_{11}H_{20}O_4$. Calc. equiv. 108.0. 0.1142 g substance: 0.0551 Ag. 0.1346 g substance: 0.0652 g Ag. Found %: Ag 48.24, 48.44.* $C_{11}H_{18}O_4Ag_2$. Calc. %: Ag 50.02.

<u>Splitting HCl from the chloride (IV)</u>. 12.2 g of the chloride (IV) was refluxed for 6 hours with 17 g of sodium ethylate in 30 ml of ethyl alcohol. The reaction product was diluted with 80 ml of water, extracted with ether, and dried over $MgSO_4$. Repeated fractionation yielded 4.8 g of a hydrocarbon.

B.p. 46.5-48.5 at 10 mm; $n_D^{20}$ 1.4446; $\omega_{FCD}$ 20.6; $d_4^0$ 0.8189; $d_4^{20}$ 0.8023; $MR_D$ 50.38; Calc. 50.33.

0.1218 g substance: 0.3935 g $CO_2$; 0.1417 g $H_2O$. 0.1279 g substance: 0.4024 g $CO_2$; 0.1481 g $H_2O$. Found %: C 86.91, 86.70; H 13.02, 12.96. 0.0456 g subs.: 17.30 g benzene; $\Delta$t 0 110°. 0.0548 g substance; 17.30 g benzene: $\Delta$t 0.110°. Found: M 145.8, 145.0. $C_{11}H_{20}$. Calc. %: C 86.84; H 13.5 M 152.

Ozonization of the hydrocarbon yielded 2-isopropylcyclopentanone. The melting point of the ketone's semicarbazone was 119°.

0.0786 g substance: 15.5 ml $N_2$ (19.3°, 758.5 mm). 0.1080 g substance: 21.3 ml $N_2$ (19.2°, 758.5 mm) Found %: N 22.70, 22.86. $C_9H_{17}ON_3$. Calc. %: N 22.94.

Analysis thus clearly shows that the reaction of diisopropylcyclobutylcarbinol with concentrated hydrochloric acid expands the ring and shifts one isopropyl group from the 1 position to the 2 position.

<div align="center">SUMMARY</div>

1. The following compounds have been synthesized and identified for the first time: diisopropylcyclobutylcarbinol; 1,1-diisopropylcyclopentanol-2; diisopropylmethylenecyclobutane; 1,1-diisopropylcyclopentene-2; 1,2-diisopropyl-1-chlorocyclopentane; and 1,2-diisopropylmethylenecyclopentane.

2. It has been shown that the reaction of diisopropylcyclobutylcarbinol with sulfuric acid follows two lines: 1) dehydration without any isomerization; and 2) dehydration with the production of an isomeric alcohol — 1,1-diisopropylcyclopentanol-2.

---

*The low percentage of Ag is due to failure to wash the silver salt of the acid with ether.

3.  Three compounds are formed in the reaction of diisopropylcyclobutyl-
carbinol with hydrochloric acid: 1,1-diisopropylcyclopentanol-2;  diisopropyl-
methylenecyclobutane;  and 1,2-diisopropyl-2-chlorocyclopentane.

4.  1,1-Diisopropylcyclopentanol-2 is dehydrated by sulfuric acid as well
as by hydrochloric acid, yielding 1,1-diisopropylcyclopentene-2, the reaction
with the latter acid also yielding two five-membered cyclic chlorides, one of
them apparently the product of a secondary reaction.

5.  The isomerization of one ring compound into another in an organomagnesium
synthesis has been observed for the first time.  In the synthesis of diisopropyl-
cyclobutylcarbinol, for example, 1,1-diisopropylcyclopentanol-2 is formed at the
same time.  The formation of the isomeric alcohol must be the result of iso-
merization of the organomagnesium complex.

## LITERATURE CITED

[1]  N. M. Kizhner, J. Russ. Chem. Soc. 40, 676 (1908); 42, 1211 (1910);
40, 1002 (1908); 41, 1351 (1909); 37, 509 (1905); 37, 517 (1905); 43, 1149
(1911).

[2]  N. Ya. Demyanov, J. Russ. Chem. Soc. 43, 840 (1911); 46, 52 (1914).

[3]  Ibid., 42, 416, 844 (1910); 37, 621 (1905); 39,671 (1907); 39, 1077,
1085, 1466 (1907).

[4]  Ibid., 42, 837 (1910).

[5]  G. G. Tatevosyan and M. S  Melikyan, J. Gen. Chem. 17, 5 (1947).

[6]  B. A. Kazansky, J. Gen. Chem. 6, 11 (1936).

[7]  Lipp, Lieb. Ann., 499, 1 (1932).

[8]  N. M. Kizhner, J. Russ. Chem. Soc. 42, 1227 (1910).

[9]  T. A. Favorskaya and the student Sh. A. Fridman, J. Gen. Chem. 15,
421 (1945).

[10]  T. A. Favorskaya, J. Gen. Chem. 17, 541 (1947).

[11]  T. A. Favorskaya and Sh. A. Fridman, J. Gen. Chem. 20, 581 (1950).[*]

---

[*] See C.B. English translation, p. 437.

# RESEARCH ON TERTIARY ALCOHOLS CONTAINING A CYCLOBUTYL RADICAL

## II. THE REACTION OF METHYLPHENYLCYCLOBUTYLCARBINOL WITH HYDROCHLORIC
## AND SULFURIC ACIDS

T. A. Favorskaya and I. P. Yakovlev

In our preceding report [1] we showed that sulfuric and hydrochloric acids dehydrate diisopropylcyclobutylcarbinol and also isomerize it to a five-membered ring. It was also found that the formation of the normal reaction product in the synthesis of diisopropylcyclobutylcarbinol from the ethyl ester of cyclobutanecarboxylic acid is paralleled by the formation of its isomeric alcohol — 1,1-diisopropylcyclopentanol-2 — as the result of isomerization of the organomagnesium complex itself.

After dealing with diisopropylcyclobutylcarbinol we decided to investigate the reaction of tertiary alcohols that contained a phenyl radical and a cyclobutyl radical with hydrochloric and sulfuric acids. In alcohols of this structure one of the transformations suffered by the alcohols was eliminated, i.e. the formation of a phenyl group, which facilitated proof of the structure of the resultant products. Three such alcohols were chosen for our research: methylphenylcyclobutylcarbinol, ethylphenylcyclobutylcarbinol and isopropylphenylcyclobutylcarbinol.

Methyl cyclobutyl ketone was synthesized by N. M. Kizhner [2] by means of an organomagnesium synthesis from cyclobutanecarboxamide, but he failed to describe it, giving only its boiling point. Kolman and Perkin [3] synthesized it from the calcium salt of cyclobutanecarboxylic acid, the yield being poor, while Perkin and Sinkler [4] synthesized it from the acid chloride of this acid, the yield being 60-65%. Ethyl cyclobutyl ketone and isopropyl cyclobutyl ketone were synthesized by N. D. Zelinsky and his associates [5,6] by passing cyclobutane carboxylic acid with propionic and isobutyric acids over ZnO and MnO catalysts, their yields being 55 and 37% of the theoretical, respectively.

An endeavor made during the course of the present research to synthesize cyclobutyl phenylketone over a chrome-manganese catalyst, using cyclobutanecarboxylic acid and a mixture of benzoic acid and ethyl benzoate, was unsuccessful. On the other hand, the synthesis of methyl cyclobutyl ketone was successful. A mixture of 1:3 parts by volume of cyclobutanecarboxylic and acetic acids was used for catalysis. The ketone yield was 50%. The yield was raised to 63% however, when the ethyl esters of these acids were used instead of the acids themselves, the proportions remaining the same. The reaction was as follows:

$$
\begin{array}{c}
CH_2 - CH_2 \\
| \quad\quad | \\
CH_2 - CH - COOC_2H_5
\end{array}
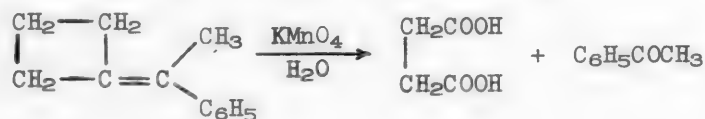+ CH_3COOC_2H_5 \longrightarrow C_4H_7COCH_3 + 2C_2H_4 + CO_2 + H_2O
$$

In our test 63% of methyl cyclobutyl ketone and 8.8% of dicyclobutyl ketone were produced in a single pass. The excess ethyl acetate yielded 40% acetone and 5% acetic acid, the rest of the ethyl acetate being recovered unchanged and being reusable without careful purification.

Methylphenylcyclobutylcarbinol was synthesized from methyl cyclobutyl ketone and phenylmagnesium bromide, but the yield was very low (9.8% of the theoretical). The principal reaction product was a saturated hydrocarbon — methylphenylmethylenecyclobutane, the yield being 17.1% of the theoretical.

$$
\begin{array}{c}
CH_2\!-\!CH_2 \\
|\qquad\ | \\
CH_2\!-\!CH\!-\!CO\!-\!CH_3
\end{array}
\xrightarrow[+H_2O]{+C_6H_5MgBr}
\begin{array}{c}
CH_2\!-\!CH_2 \\
|\qquad\ | \qquad CH_3 \\
CH_2\!-\!CH\!-\!\underset{\underset{C_6H_5}{|}}{COH}
\end{array}
+
\begin{array}{c}
CH_2\!-\!CH_2 \\
|\qquad\ | \qquad CH_3 \\
CH_2\!-\!C\!=\!C\!-\!C_6H_5
\end{array}
$$

$$(\text{I}) \qquad\qquad\qquad (\text{II})$$
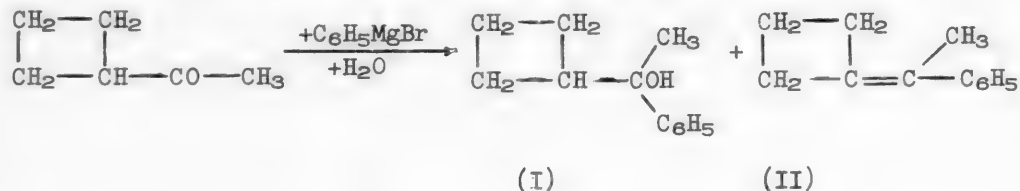
Cautious oxidation of the methylphenylmethylenecyclobutane with a $KMnO_4$ solution yielded acetophenone and succinic acid:

$$
\begin{array}{c}
CH_2\!-\!CH_2 \\
|\qquad\ | \qquad CH_3 \\
CH_2\!-\!C\!=\!C \\
\qquad\qquad\quad C_6H_5
\end{array}
\xrightarrow[H_2O]{KMnO_4}
\begin{array}{c}
CH_2COOH \\
| \\
CH_2COOH
\end{array}
+ \; C_6H_5COCH_3
$$

In view of the poor yield of methylphenylcyclobutylcarbinol, we abandoned its synthesis from methyl cyclobutyl ketone. It was synthesized otherwise: via cyclobutanecarbonyl chloride and phenyl cyclobutyl ketone.

Cyclobutanecarboxylic acid was prepared by the N. M. Kizhner method [7], as modified by Golmov and Kazansky [8], the yield being raised 14.8% in the first stage of the reaction (to 93% of the theoretical) and by 11% in the second stage (to 88% of the theoretical). The ethyl ester of cyclobutane-1,1-dicarboxylic acid was saponified and decarboxylated to give an 80% yield of cyclobutanecarboxylic acid. It was then converted into its acid chloride by the action of $PCl_5$, the yield being 78.5%. Phenyl cyclobutyl ketone was synthesized in a Friedel-Crafts reaction from the acid chloride and benzene with $AlCl_3$, the yield being 68% of the theoretical. This ketone was first synthesized by Perkin and Sinkler [9], using the same method, but their yield was 55%. The phenyl cyclobutyl ketone thus prepared served as the initial substance in our synthesis of methyl-, ethyl-, and isopropylphenylcyclobutylcarbinol.

In contrast to the synthesis of methylphenylcyclobutylcarbinol from methyl cyclobutyl ketone and phenylmagnesium bromide, synthesizing the alcohol from phenyl cyclobutyl ketone and methylmagnesium bromide produced a high yield (90% of the theoretical), no unsaturated product being formed at all. Oxidizing methylphenylcyclobutylcarbinol with a chromic acid mixture yielded acetophenone and benzoic acid.

The alcohol did not react when it was heated with 25% sulfuric acid to 90° for 6 hours. When reacted with 50% $H_2SO_4$ under the same conditions, it yielded an unsaturated hydrocarbon — methylphenylmethylenecyclobutane. Oxidation of the hydrocarbon with a $KMnO_4$ solution yielded acetophenone and a minute quantity of benzoic acid. 18% and 36% hydrochloric acid merely dehydrate the methylphenylcyclobutylcarbinol, two unsaturated hydrocarbons being produced at the same time: 80% of methylphenylmethylenecyclobutane and 20% of as-cyclobutylphenyl-

ethylene. The difference between their boiling points is slight, so that we must assume that the resultant fractions were not homogeneous, but contained slight traces of an isomeric hydrocarbon:

$$\begin{array}{ccc}
CH_2 \!\!-\!\! CH_2 & OH \\
| \qquad\quad | & | \diagup CH_3 \\
CH_2 \!\!-\!\! CH \!\!-\!\! C \diagdown \\
\qquad\qquad\qquad C_6H_5
\end{array}
\xrightarrow[36\% \text{ HCl, } 0°, 24 \text{ hours}]{18\% \text{ HCl, } 90°, 6 \text{ hours}}
\begin{array}{ccc}
CH_2 \!\!-\!\! CH_2 & CH_3 \\
| \qquad\quad | & \diagup \\
CH_2 \!\!-\!\! C \!\!=\!\! C \!\!-\!\! C_6H_5
\end{array}
+
\begin{array}{ccc}
CH_2 \!\!-\!\! CH_2 & CH_2 \\
| \qquad\quad | & \| \\
CH_2 \!\!-\!\! CH \!\!-\!\! C \!\!-\!\! C_6H_5
\end{array}$$
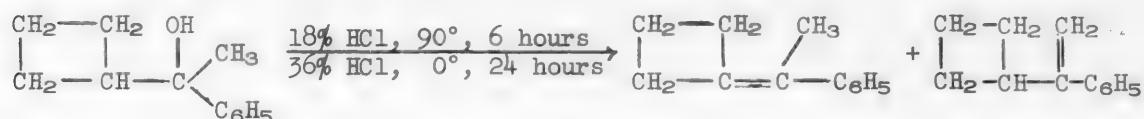
Cautious oxidation of the methylphenylmethylenecyclobutane fraction with a $KMnO_4$ solution yielded acetophenone and benzoic, succinic, and formic acids; traces of the last acid were detected by producing calomel. Ozonization of the as-cyclobutylphenylethylene yielded formic acid and phenyl cyclobutyl ketone as the principal reaction products, plus traces of acetophenone and benzoic and succinic acids.

## EXPERIMENTAL

Catalytic synthesis of methyl cyclobutyl ketone. a) Preparation of the catalyst. 36.5 ml of a 26% ammonia solution was added to 60 g of chromic anhydride, and the total volume of the solution was brought up to 300 ml by the addition of water. The resultant solution was poured into 110 g of manganic nitrate dissolved in 300 ml of water, and another 36.5 ml of the 26% ammonia solution was added. The resultant brown precipitate was filtered out, washed well with water, and dried in a thermostat at 110°, after which it was decomposed by heating over a Bunsen burner in a porcelain dish with constant stirring. The decomposition process entailed the spontaneous evolution of considerable heat. The catalyst was a dark-brown, highly mobile powder. The catalyst was deposited on glass wool. The reaction was carried out in the usual catalytic apparatus, 40 g of the catalyst being used.

b) Preparation of methyl cyclobutyl ketone. 10 ml of the ethyl ester of cyclobutane carboxylic acid and 30 ml of ethyl acetate were used in catalysis, the volumetric rate of flow being 10-12 ml per hour, and the temperature 440°. This yielded 22 ml of the catalyzate. 106 ml of the ethyl ester of cyclobutane-carboxylic acid and 350 ml of ethyl acetate were processed in the same way, yielding 80 ml of acetone, 62 ml of ethyl acetate, 3 ml of acetic acid, 5 ml of the ethyl ester of cyclobutanecarboxylic acid, 60 g of methyl cyclobutyl ketone (63% of the theoretical), and 5 g of dicyclobutyl ketone.

Methyl cyclobutyl ketone was a mobile liquid with a yellowish tint and a peculiar odor.

B.p. 137-139° at 754 mm, 36° at 11 mm; $n_D^{10}$ 1.4339; $\omega_{FCD}$ 21.1; $d_4^{10}$ 0.9093; $MR_D$ 28.06; Calc. 27.72.

0.0844 g substance: 0.2256 g $CO_2$, 0.0829 g $H_2O$. 0.0649 g substance: 0.1756 g $CO_2$, 0.0652 g $H_2O$. Found %: C 73.95, 73.83; H 10.77, 10.98. $C_6H_{10}O$. Cal. %: C 73.47; H 10.20.

Semicarbazone m.p. 135.5°.

0.0590 g substance: 13.7 ml $N_2$ (18.1°, 768 8 mm). Found %: N 27.64. $C_7H_{13}ON_3$. Cal % N 27.09.

Synthesis of methylphenylcyclobutylcarbinol from methyl cyclobutyl ketone. 80 g of bromobenzene in 80 ml of absolute ether was slowly added to 12.4 g of magnesium, the flask being chilled with water containing snow. When all the magnesium had dissolved, a solution of 50 g of methyl cyclobutyl ketone in 200

ml of ether was added. The next day the organomagnesium complex was decomposed with water, the ether layer decanted and dried over $MgSO_4$, the residue acidulated with dilute (1:5) hydrochloric acid and extracted with ether, and the ether extract washed with water and dried over $K_2CO_3$ The two ether extracts were combined, the ether driven off on a water bath, and the residual oil fractionated. Repeated fractionation into a heated 50-cm herringbone dephlegmator and freezing the resultant diphenyl yielded 16.5 g of an unsaturated hydrocarbon and 10 g of an alcohol.

The unsaturated hydrocarbon — methylphenylmethylenecyclobutane — was a mobile liquid with a slight tarry odor:

B.p. 80-83° at 0.5 mm; $n_D^{12.5}$ 1.5551; $\omega_{FCD}$ 36.65; $d_4^0$ 0.9859; $d_4^{12.5}$ 0.9743; $d_4^{20}$ 0.9683; $MR_D$ 52.06; Calc. 51.81.

0.1192 g substance: 16.70 g benzene: $\Delta t$ 0.232°. Found: M 154.9. $C_{12}H_{14}$. Calc. M 158.0.

0.1429 g substance: 0.4743 g $CO_2$; 0.1147 g $H_2O$. 0.1422 g substance: 0.4749 g $CO_2$; 0.1132 g $H_2O$. Found %: C 90.58, 91.13; H 8.78, 8.56. $C_{12}H_{14}$. Calc. %: C 91.14; H 8.86.

Oxidation of the hydrocarbon with potassium permanganate yielded acetophenone and succinic acid. The m.p. of the acetophenone's semicarbazone was 200° its mixed melting point with a known preparation exhibiting no depression. The succinic acid had a m.p. of 182°, its mixed melting point likewise not exhibiting any depression.

The alcohol — methylphenylcyclobutylcarbinol — was a liquid with a slight tarry odor after treatment with a $KMnO_4$ solution.

B.p. 100.5-104° at 1 mm; $n_D^{20}$ 1.5358; $\omega_{FCD}$ 27.5; $d_4^0$ 1.0388; $d_4^{10}$ 1.0350; $d_4^{20}$ 1.0316; $MR_D$ 53.72, 53.80.

0.0573 g substance; 17.45 g benzene: $\Delta t$ 0.094°. 0.0455 g subs.: 17.45 g benzene: $\Delta t$ 0.079°. Found: M 176.0, 163.0. $C_{12}H_{16}O$. Calc. M 178.0. 0.1713 g substance: 0.5143 g $CO_2$; 0.1383 g $H_2O$. 0.1727 g substance: 0.5186 g $CO_2$; 0.1409 g $H_2O$. Found %: C 81.93, 81.95; H 8.63, 8.92. $C_{12}H_{16}O$. Calc. %: C 81.76; H 9.15.

Synthesis of cyclobutanecarboxylic acid by the Kizhner method [7]. Synthesis of cyclobutanecarboxylic acid required the preparation of 1-bromo-3-chloro-propane, malonic ester, and absolute ethyl alcohol. The reaction was carried out in stages as proposed by Golmov and Kazansky [8]. In view of the fact that our yields were better than those obtained by the foregoing authors,* we shall describe the conditions employed in our synthesis. The first stage of the synthesis was synthesizing the ethyl ester of $\gamma$-chloropropylmalonic acid. A mixture of 3 mols of malonic ester and 3 mols of 1-bromo-3-chloropropane in 500 ml of absolute ether was added in one batch to sodium ethylate, prepared from 2 mols of metallic sodium and 800 ml of absolute alcohol. The temperature of the reaction mixture was kept at 35° for four hours, and then the reaction mixture was set aside to stand for a day at room temperature (17-18°) after which 2.5 liters of water were added to the unacidulated reaction product. The oil layer was separated, and the residue extracted with ether. The oil and the ether extract were combined, washed with water, dried over $Na_2SO_4$, and fractionated. This yielded 93% of the theoretical yield (as against 78.5% secured by Golmov and Kazansky) of $\gamma$-chloropropylmalonic ester, with a b.p.

---

*The difference between our method and that of Golmov and Kazansky involve differing reaction temperature as well as a certain change in the principles of processing and isolating the reaction products.

of 142° at 10 mm. The ester was poured in one batch into a solution of sodium alcoholate in 250 ml of absolute alcohol heated to 80° (on the basis of 1 mol of sodium per mol of the ester), most of the alcohol being distilled at once on a water bath. The residue was dissolved in water and acidulated with hydrochloric acid, and the ethyl ester of cyclobutanedicarboxylic acid was extracted with ether. The yield was 88% of the theoretical (as against the 77% secured by Golmov and Kazansky).

The ethyl ester of cyclobutane-1,1-dicarboxylic acid was saponified with a 40% NaOH solution. After the resultant mixture had been acidulated and the acid recovered, it was decarboxylated by double distillation at atmospheric pressure. The overall yield after all three operations was 90% of the theoretical.

Synthesis of cyclobutanecarbonyl chloride. 490 g of cyclobutanecarboxylic acid was added a drop at a time to 1.1 kg of freshly prepared $PCl_5$. When the reaction, which occurred readily, was over, the reaction product was fractionated into a column in vacuo. Cyclobutanecarbonyl chloride is a highly mobile liquid with a sharp, disagreeable odor, b.p. 52-54° at 40 mm. The yield of the acid chloride was 456 g, or 78.5% of the theoretical.

Synthesis of phenyl cyclobutyl ketone. 100 g of cyclobutanecarbonyl chloride was added a drop at a time to 200 g of $AlCl_3$ in 750 ml of freshly distilled benzene. The reaction set in at 25°. The temperature of the reaction mass was gradually raised to 60° and kept there until no more HCl was liberated. After the reaction mass had cooled, the product was cautiously poured over snow and extracted with benzene, the benzene extract being washed with a soda solution and dried over $CaCl_2$ The benzene was then driven off, and the residual oil distilled with steam. The resulting ketone was distilled. B.p. 121.5-122° at 10 mm; $n_D^{20}$ $^5$ 1.5472; $\omega_{FCD}$ 33.8; $d_4^0$ 1.0610; $d_4^{10}$ 1.0525; $d_4^{20}$ 1.0440; $MR_D$ 48.61; Calc. 47.67.

456 g of the acid chloride yielded 310 g of the ketone, or 68% of the theoretical. The ketone is a mobile canary-yellowish liquid with a pleasant odor, in low concentrations resembling that of geraniums. An ether solution of the ketone reacts exothermally with bromine, yielding a monobromo derivative with a m.p. of 61°. It slightly decolorized a solution of potassium permanganate. It does not color a ferric chloride solution. Reacted with semicarbazide it yields a semicarbazone with a m.p. of 177°.

0.2114 g substance: 0.1657 g AgBr. 0.1932 g substance: 0.1511 g AgBr. Found %: Br 33.35, 33.28. $C_{11}H_{11}BrO$. Calc. %: Br 33.46. 0.0963 g substance: 16.0 ml $N_2$ (19.5°, 758.0 mm). 0.0815 g substance: 13.8 ml $N_2$ (19.5°, 755.8 mm). Found %: N 19.35, 19.65. $C_{12}H_{15}ON_3$. Calc. %: N 19.35.

Synthesis of methylphenylcyclobutylcarbinol from phenyl cyclobutyl ketone. A solution of 20 g of methyl bromide in 200 ml of absolute ether was added portionwise from a dropping funnel, with efficient chilling and stirring, to 9.2 g of magnesium. Another 20 g of methyl bromide was passed through the solution of the organomagnesium compound as a gas. A solution of 60 g of phenyl cyclobutyl ketone in 100 ml of ether was then added drop by drop to the resultant methylmagnesium bromide, the resultant organomagnesium complex not dissolving in the ether. After all the solution had been added, the reaction mass was stirred for another 2.5 hours at room temperature, no heat being applied, and then decomposed with pieces of ice. The ether layer was decanted. The residue was acidulated with weak hydrochloric acid and extracted with ether, the ether extract being washed with a soda solution and with water, combined with the bulk of the ether layer, dried over $Na_2SO_4$, and fractionated. The constants

of the alcohol thus produced were exactly the same as those of the alcohol prepared from methyl cyclobutyl ketone and phenylmagnesium bromide; no unsaturated product was found in the alcohol. The yield was 59 g, or 90% of the theoretical.

Oxidation of methylphenylcyclobutylcarbinol by a chromic acid mixture. 50 g of potassium bichromate, 60 g of sulfuric acid (sp. gr. 1.84), and 200 ml of water were used in oxidizing 10 g of the alcohol. Oxidation was effected by adding the chromic acid mixture to the alcohol a drop at a time. The reaction set in at 60-67° and continued at that temperature for 3 hours. Then the reaction mixture was chilled, diluted with 200 ml of water, and extracted thoroughly with ether. The ether extract was washed with alkali and dried over $MgSO_4$. The alkali solution was acidulated with an excess of dilute (1:5) sulfuric acid and extracted with ether, the ether extract being washed with 20 ml of water and dried over $MgSO_4$. Driving off the ether from the ether extract followed by fractionation yielded 1.2 g of acetophenone (b.p. 71-74° at 8 mm). The acetophenone yielded a semicarbazone with a m.p. of 200°, its mixed melting point with the known semicarbazone exhibiting no depression. The acid portion of the reaction mixture yielded 0.6 g of benzoic acid with a m.p. of 121°, its mixed melting point with known benzoic acid exhibiting no depression.

Reaction of methylphenylcyclobutylcarbinol with $H_2SO_4$. a) A mixture of 15 g of the alcohol with 15 ml of 25% $H_2SO_4$ was heated to 90° for 6 hours, the reaction product turning slightly brown. It was extracted with ether, washed with a soda solution, and dried over $MgSO_4$. After the ether had been driven off, the 11 g of residue was distilled at 8 mm, all the product passing over in the 97-106° range. The residue of 0.5 g was not analyzed. $n_D^{19}$ 1.5629; $\omega_{FCD}$ 37.8; $d_4^{19}$ 0.9771; $MR_D$ 52.53; $C_{12}H_{14}$; Calc. 51.81. The physical constants of the distilled unsaturated hydrocarbon and its chemical behavior were those of the hydrocarbon secured in the organomagnesium synthesis of the alcohol from methyl cyclobutyl ketone and phenylmagnesium bromide.

Two fractions were secured after redistillation (at 8 mm): I) b.p. 98-101°, 4.6 g; and II) b.p. 101-102°, 3.5 g.

Fraction I. $n_D^{20}$ 1.5619; $\omega_{FCD}$ 36.6; $d_4^{20}$ 0.9695; $MR_D$ 52.84; Calculated 51.81. 0.0477 g substance; 16.65 g benzene: $\Delta$ t 0.090° 0.0804 g substance; 16.65 g benzene: $\Delta$ t 0.156° Found: $\underline{M}$ 160.0, 155.8. $C_{12}H_{14}$. Calculated: $\underline{M}$ 158.0.

Fraction II. $n_D^{20}$ 1.5650; $\omega_{FCD}$ 38.0; $d_4^{20}$ 0.9799; $MR_D$ 52.52; Calculated 51.81.

0.1784 g substance: 0.5936 g $CO_2$; 0.1358 g $H_2O$. 0.1902 g substance: 0.6384 g $CO_2$; 0.1560 g $H_2O$. 0.0402 g substance; 16.15 g benzene: $\Delta$ t 0.078° 0.0780 g substance: 16.15 g benzene: t 0.151. Found %: C 90.82, 91.45; H 8.53, 9.17. $\underline{M}$ 160.2, 160.5. $C_{12}H_{14}$. Calculated %: C 91.14; H 8.86. $\underline{M}$ 158.
Oxidizing Fractions I and II with a $KMnO_4$ solution yielded acetophenone and benzoic acid. The acetophenone semicarbazone fused at 198.5° The mixed melting points of the semicarbazone and the benzoic acid with the respective known compounds exhibited no depression.

Reaction of methylphenylcyclobutylcarbinol with 18% hydrochloric acid. 15 g of the alcohol was heated to 85° for 6 hours with 20 ml of an 18% solution of hydrochloric acid. The slightly brown reaction product was extracted with ether, washed with a soda solution, and dried over $Na_2SO_4$. Distillation yielded two fractions (at 8 mm): I) b.p. 98-100°, 8.4 g; and II) b.p. 115-122°, 4.4 g. Fraction II was

a mixture of an unsaturated hydrocarbon and the original alcohol. Fraction I was an unsatured hydrocarbon, a highly mobile, colorless liquid with a faint odor of spruce tar: $n_D^{20}$ 1.5585; $\omega_{FCD}$ 36.6; $d_4^{20}$ 0.9672; $MR_D$ 52.71; $C_{12}H_{14}$. Calculated. 51.81. The hydrocarbon was combined with the Fraction I secured in the reaction of the alcohol with 36% hydrochloric acid.

Reaction of methylphenylcyclobutylcarbinol with 36% hydrochloric acid. 16.5 g of the alcohol was poured into 36% hydrochloric acid chilled to 0° and allowed to stand at this temperature for 24 hours. Then the floating oil was removed in a separatory funnel, the acid residue being diluted with 100 ml of water and extracted with ether. The ether extract was combined with the separated oil, and the whole was washed with 20 ml of water and dried over $MgSO_4$. Driving off the ether and fractionating the residue at 8 mm yielded two fractions: I) b.p. 95-106°, 6 g; and II) b.p. 106-109°, 6.1 g.

Fraction I was combined with the hydrocarbon secured in the reaction with the 18% hydrochloric acid. Careful fractional distillation at 9 mm yielded two hydrocarbons: I) b.p. 98-100°, 12.5 g, and II) b.p. 105-107°, 3.3 g; plus III) (an intermediate fraction with a b.p. of 100-105°), 4.5 g.

Both of the hydrocarbons (Fractions I and II) were mobile, colorless liquids with the odor of fresh spruce tar

Fraction I. $n_D^{21.5}$ 1.5575; $\omega_{FCD}$ 36.8; $d_4^{21.5}$ 0.9608; $MR_D$ 52.98; Calculated. 51.81.

0.1213 g substance: 0.4048 g $CO_2$; 0.0986 g $H_2O$. 0.1034 g substance; 0.3441 g $CO_2$; 0.0833 g $H_2O$. 0.0350 g substance; 17.35 g benzene: $\Delta t$ 0.065°. 0.0648 g substance; 17.35 g benzene: $\Delta t$ 0.117°. Found %: C 90.98, 90.86; H 9.08, 9.01. M 156.3, 160.4. $C_{12}H_{14}$. Calculated %: C 91.14; H 8.86. M 158.0.

Fraction II. $n_D^{21}$ 1.5608; $\omega_{FCD}$ 37.6; $d_4^{21}$ 0.9838; $MR_D$ 51.98; Calculated 51.81.

0.1018 g substance; 0.3401 g $CO_2$; 0.0829 g $H_2O$. 0.1664 g substance; 0.5541 g $CO_2$; 0.1293 g $H_2O$. 0.0417 g substance; 17.05 g benzene: $\Delta t$ 0.077. 0.0738 g substance; 17.05 g benzene: $\Delta t$ 0.143. Found %: C 91.05, 90.70; H 9.11, 8.75. M 159.7, 152.1. $C_{12}H_{14}$ Calculated %: C 91.14; H 8.86. M 158.0.

Oxidizing Fraction I with a $KMnO_4$ solution yielded acetophenone and benzoic, formic, and succinic acids. The formic acid was detected by the formation of traces of calomel. 10 g of the hydrocarbon in 200 ml of water was used in the reaction. The $KMnO_4$ was added in small batches as it was consumed, oxidation consuming 30 g of $KMnO_4$, instead of the calculated 32.5 g. The 4.5 g of acetophenone yielded a semicarbazone with a m.p. of 201.5°. The mixed melting points of the semicarbazone, the benzoic acid, and the succinic acid with the respective known compounds exhibited no depression.

Fraction II was ozonized in chloroform, 2.8 g of the hydrocarbon being used for ozonization. After the ozonization reaction was complete, the chloroform was drawn off in vacuum. The ozonide was decomposed with water, first at room temperature and then by heating with a reflux condenser. A test with fuchsin-sulfurous acid for formaldehyde was negative. Then a solution of 4 g of soda in 10 ml of water was added to the ozonization product, and the resultant solution was boiled. The volatile products were distilled with steam (1.2 g), yielding 0.4 g of acetophenone with a b.p. of 78 at 10 mm. The semicarbazone of the

acetophenone, m.p. 200°, exhibited no depression when mixed with the known semicarbazone. The distillation residue of 0.8 g formed a weak silver mirror, and hence was processed with moist silver oxide by the Delepine method [10] But this treatment failed to produce a positive result, since the appropriate processing yielded nothing but phenyl cyclobutyl ketone. Its semicarbazone, with a m.p. of 176°, exhibited no depression of the melting point with the known semicarbazone.

The acid products yielded benzoic acid, m.p. 120°. Distillation with steam yielded formic acid. A reaction of the first runnings of formic acid with mercuric chloride yielded an abundant precipitate, which yielded an abundant black precipitate, in turn, when a strong NaOH solution was added. After the benzoic and formic acids had been eliminated, the residue yielded succinic acid with a m.p. of 181°. The mixed melting points of the succinic and benzoic acids with the respective known compounds exhibited no depression.

## SUMMARY

1. Methylphenylcyclobutylcarbinol and its dehydration products – as-phenyl-cyclobutylethylene and methylphenylmethylenecyclobutane – have been synthesized for the first time

2. It has been shown that the reaction of methylphenylcyclobutylcarbinol with hydrochloric and sulfuric acids results only in its dehydration.

3. The catalytic synthesis of methyl cyclobutyl ketone from the acids and esters of the acids has been worked out, the yields running up to 63%.

4. It has been found that the yield of methylphenylcyclobutylcarbinol from phenyl cyclobutyl ketone is practically quantitative, though its yield from methyl cyclobutyl ketone is only 10%.

5. The synthesis of cyclobutanecarboxylic acid has been improved, the product yields being 93, 88, and 90% in the different reaction stages.

6. It has been found that dehydration of methylphenylcyclobutylcarbinol with sulfuric acid affects the cyclobutyl radical, dehydration with hydrochloric acid affecting the methyl group.

## LITERATURE CITED

[1] T. A. Favorskaya and I. P. Yakovlev, J. Gen. Chem., 22, 113 (1952).

[2] N.M. Kizhner, J. Russ. Chem. Soc. 45, 245, 973 (1911).

[3] Kolman and Perkin, J. Chem. Soc., 51, 229 (1887).

[4] Perkin and Sinkler, J. Chem. Soc., 61, 47 (1892).

[5] N. D. Zelinsky and B A. Kazansky, J. Russ. Chem. Soc. 59, 659 (1927); Zelinsky and Rashina, Ber., 57, 1932 (1924).

[6] N. D. Zelinsky and Gutt, Ber., 41, 2432 (1908).

[7] N. M. Kizhner, J. Russ. Chem. Soc. 42, 1230 (1910).

[8] V. P. Golmov and B. A. Kazansky, Proc. USSR Acad. Sci. 33, 37 (1927).
[9] Perkin, Sinkler, J.Chem.Soc., 61, 59 (1892).

[10] Delepine, Bonnet, Comptes rend., 149, 39; Chem. Zentr., 1909, II, 589.

# THE REACTIONS OF GLYCIDOL AND ITS ETHERS WITH ACID AMIDES

## III.  REACTION OF GLYCIDOL ETHERS WITH ACETAMIDE

### F. D. Ponomarev

Our preceding report [1] described the reaction of glycidol methyl and ethyl ethers with formamide, showing that these glycidol ethers react with formamide to yield the respective N-mono- and N,N-disubstitution derivatives of formamide.  In the present report we describe the reactions of glycidol methyl and ethyl ethers with acetamide and the properties of the resultant products.

The experiments on the reaction of acetamide with these ethers were carried out at various temperatures, with heat applied for different lengths of time, with and without acid ($H_2SO_4$) and basic (NaOH) catalysts, with acetamide-ether ratios of 1:1, 1:2, and 2:1, and with refluxing over an oil bath or heating in sealed ampoules.

The reaction hardly takes place at all when refluxing is done at 100-130° for 5 hours.  Nor does a 100%, or even a 200%, excess of acetamide produce a satisfactory result.  It was found that the reaction of acetamide with glycidol ethers occurs best under pressure in sealed glass ampoules.  Under these conditions two products are formed as a rule:  N-mono- and N,N-disubstitution derivatives of acetamide and its polymer.  There were no advantages in carrying out the reaction in toluene.  Nor was any advantage found in experiments in which the ether was used in excess (2 mols) or when prolonged heating (12 hours) was employed.  These conditions, as well as a higher temperature (165°), result in a decrease in the product yield and an increase in the polymer yield.

It should be noted that acetamide does not react with glycidol ethers as readily as does formamide.  The best results were usually secured in the reaction of acetamide with the glycidol ethers when the following procedure was used.  The acetamide was placed in a refractory tube with a 20% excess of the glycidol ether over the theoretical and 2-3 drops of NaOH.  The tube was sealed and heated on an oil bath at 150° for 10 hours.  When the tube was opened, no gaseous products were found, as a rule. After this heating period, the reaction mixture was an oily, homogeneous, light or dark-brown liquid.  Chilling it (to -10°) caused part of the unreacted amide to settle out;  it was filtered out, and the reaction mixture was processed three times with ether (25-ml batches) to eliminate the amide completely.  Then the ether was driven off on a water bath, and the reaction product was vacuum-distilled two or three times.  In every case a residue (18-20%) was left within the flask as a faintly or brightly colored polymer after the reaction product had been distilled.

All the alkoxy hydroxy amides we produced were liquids with a specific odor, which were freely soluble in alcohol and ether.  The constants of the synthesized substances are given in the table.

| Substance | Boiling Point at 8 mm | $d_4^{15}$ | $n_D^{15}$ | $MR_D$ Calc. | $MR_D$ Found |
|---|---|---|---|---|---|
| $CH_3CONH-CH_2-CHOH-CH_2OCH_3$ | 97–105° | 1.0876 | 1.4461 | 36.69 | 36.09 |
| $CH_3CONH-CH_2-CHOH-CH_2OC_2H_5$ | 122–125 | 1.0605 | 1.4450 | 41.19 | 40.41 |
| $CH_3CON(CH_2-CHOH-CH_2OCH_3)_2$ | 158–165 | 1.0775 | 1.4482 | 58.87 | 58.46 |
| $CH_3CON(CH_2-CHOH-CH_2OC_2H_5)_2$ | 165–170 | 1.0524 | 1.4471 | 67.90 | 66.91 |

We have also investigated the reactions of these glycidol ethers with ethane-sulfonamide and benzenesulfonamide. Experiments with these amides, run under various conditions, like those with acetamide, either failed to yield any satis-factory results at all or else, when we did manage to isolate the N-mono- or N,N-disubstitution derivative of ethanesulfonamide, the minute quantities obtained made it impossible to identify them in detail (the percentage of nitrogen was determined by the Kjeldahl method).

One of the outstanding chemical properties of N-mono- and N,N-disubstitution derivatives of acetamide is their instability. They turn yellow in storage, decomposing, even though only slowly. Their decomposition is quicker when they are acted upon by solid alkalies at room temperature, the sharp odor of ammonia being manifested, particularly when the products are distilled over solid KOH in vacuo.

## EXPERIMENTAL

A commercial preparation of acetamide (m.p. 80°) was employed in the re-action; the glycidol ethers were prepared from glycerol by the method described in the preceding communication [1], the sole change being that the ethers of glycerol α-monochlorohydrin were prepared with a boron fluoride etherate as a catalyst by the method described by A. A. Petrov [2] for synthesizing the methyl ether of glycerol α-monochlorohydrin. An 800% excess of absolute methanol or ethyl alcohol and 0.5-0.8 mg of boron fluoride etherate were added to 0.2 mol of epichlorohydrin (b.p. 115-119°) chilled to -10°. The bottle was left to stand in the -10° freezing mixture. After 2 hours had elapsed, the contents of the bottle were fractionated with a three-bulb dephlegmator. The reaction is thus 4 to 5 times faster when $BF_3 \cdot (C_2H_5)_2O$ is present than when $H_2SO_4$ is used, and the yields of the glycerol chloro ethers are higher: 77.5% of the methyl ether and 71% of the ethyl ether. These ethers were then converted into the respec-tive glycidol ethers by the use of a solid caustic alkali (in absolute ether).

1. Reaction of glycidol methyl ether with acetamide. 3.6 g of acetamide, 6.5 g of the ether (20% excess), and 3 drops of the catalyst — conc. NaOH — were heated together in a sealed tube to 140-150° on an oil bath for 10 hours. The reaction mixture was chilled to -10° to precipitate the unreacted acetamide. The precipitated amide was filtered out, and then the reaction product was pro-cessed three times with absolute ether, using 25 ml at a time, which threw down a little more of the amide. A total of 1.04 g (30%) of the acetamide was thus recovered unchanged. After the ether had been driven off on a water bath, the reaction product was twice fractionated in vacuo, yielding 3.9 g (36%) of N-propanol-2-methoxy-3-acetamide, 2.9 g (33.7%) of N,N-di-(propanol-2-methoxy-3)--acetamide, and 2.8 g of a polymer.

Experiments run under similar conditions with toluene or at a somewhat

higher temperature (165° instead of 140-150°) manifested no advantages. It should be added that acetamide did not react with glycidol ethers at all when the NaOH catalyst was absent.

The resultant products — the N-mono and N,N-disubstitution derivatives of acetamide — are oily, light-yellow liquids with a faint specific odor, freely soluble in alcohol, acetone, and ether.

### Analysis of N-propanol-2-methoxy-3-acetamide.

0.1112 g subs.: 7.54 ml 0.1 N $H_2SO_4$ (Kjeldahl method); 0.1358 g subs.: 9.26 ml 0.1 N. $H_2SO_4$; 0.1494 g subs.: 0.2354 g AgI (Zeisel method). Found %: N 9.49, 9.47; $CH_3O$ 20.79. $C_6H_{13}O_3N$. Calc. %: N 9.52; $CH_3O$ 21.07.

### Determination of the number of hydroxyl groups.

A weighed sample was heated on a boiling water bath for 4 hours with a titrated mixture of acetic anhydride and pyridine (10%), the excess acetic acid being back-titrated with a 0.1N solution of alkali after the reaction mixture had been poured into water.

0.1204 g subs.: 8.14 ml 0.1 N NaOH; 0.1314 g subs.: 8.68 ml 0.1 N. NaOH. Found %: OH 11.49, 11.22. $C_6H_{12}O_2(OH)N$. Calc. %: OH 11.56.

### Analysis of N,N-di-(propanol-2-methoxy-3)-acetamide.

0.1107 g subs.: 4.58 ml 0.1 N $H_2SO_4$ (Kjeldahl method); 0.1169 g subs.: 4.75 ml 0.1 N $H_2SO_4$; 0.1192 g subs.: 0.2474 g AgI (Zeisel method); 0.1154 g subs.: 9.63 ml 0.1 N NaOH; 0.1203 g subs.: 9.98 ml 0.1 N. NaOH. Found %: N. 5.80, 5.68; $CH_3O$ 27.38; OH 14.18 14.10. $C_{10}H_{19}O_3N(OH)_2$. Calc. %: N. 5.95; $CH_3O$ 27.23; OH 14.46.

In addition to the N-mono and N,N-disubstitution derivatives of acetamide, the high-boiling fraction yielded a small quantity of a thick, oily liquid with the following constants:

B.p. 200-211° at 6 mm; $d_4^{15}$ 1.094; $n_D^{15}$ 1.4460.

0.1460 g subs.: 4.18 ml 0.1 N $H_2SO_4$ (Kjeldahl method). Found %: N 4.01. $C_{18}H_{37}O_9N$. Calc. %: N 3.49.

To judge from the analytical data, this substance apparently is a product of the reaction of the N,N-disubstitution derivative of acetamide with two more molecules of the ether. The product was not analyzed further.

2. Reaction of glycidol ethyl ether with acetamide. The reaction of 7.15 g (0.07 mol) of the ethyl ether with 3 g (0.05 mol) of acetamide in the presence of 1-3 drops of NaOH under the conditions specified above yielded 3.2 g (26.4%) of N-propanol-2-ethoxy-3-acetamide, 1 g (10%) of N,N-di-(propanol-2-ethoxy-3)--acetamide, a fraction with a b.p. of 220-230° at 6 mm, and 1.5 g of a polymer. As in the experiments with the glycidol methyl ether, 20 to 30% of the unreacted acetamide was recovered.

### Analysis of N-propanol-2-ethoxy-3-acetamide.

0.1198 g subs.: 7.45 ml 0.1 N $H_2SO_4$ (Kjeldahl method); 0.1234 g subs.: 7.58 ml 0.1 N $H_2SO_4$; 0.1168 g subs.: 0.1717 g AgI (Zeisel method); 0.1246 g subs.: 7.61 ml 0.1 N NaOH; 0.1188 g subs.: 7.20 ml 0.1 N NaOH. Found %: N 8.70, 8.60; $C_2H_5O$ 28.23; OH 10.38, 10.30. $C_7H_{14}O_2N(OH)$. Calc. %: N 8.69; $C_2H_5O$ 27.92; OH 10.55.

<u>Analysis of N,N-di-(propanol-2-ethoxy-3)-acetamide</u>.

0.1258 g subs.: 4.32 mg 0.1 N $H_2SO_4$ (Kjeldahl method); 0.1125 g
subs.: 3.82 ml 0.1 N $H_2SO_4$; 0.0738 g subs.: 0.2971 g AgI (Zeisel
method); 0.1145 g subs.: 7.95 ml 0.1 N. NaOH; 0.1056 g subs.: 7.21
ml 0.1 N. NaOH. Found %: N 4.80, 4.75; $C_2H_5O$ 32.84; OH 11.80, 11.60.
$C_{12}H_{23}O_3(OH)_2N$. Calc. %: N 5.32; $C_2H_5O$ 34.19; OH 12.91.

Analysis of the fraction with a b.p. of 220-230° at 6 mm: $d_4^{20}$ 1.0697;
$n_D^{20}$ 1.4620; $MR_D$ 120.10; Calc. 120.42.

0.1559 g subs.: 3.48 ml 0.1 N. $H_2SO_4$ (Kjeldahl method). Found %:
N 3.12. $C_{22}H_{45}O_5N$. Calc. %: N 2.99.

As far as can be judged from the data cited, the synthesized substance
apparently is a condensation product of a N,N-disubstitution derivative of aceta-
mide with two more molecules of the glycidol ether. The product was a thick,
oily liquid with a specific acrid odor. The substance was not investigated any
further.

    3. <u>Reaction of glycidol methyl ether with ethanesulfonamide</u>. The reaction
of 5.6 g of ethanesulfonamide (m.p. 58°) with 9.0 g (2 mols) of glycidol methyl
ether in the presence of 4 drops of conc. NaOH under the conditions specified
above yielded 1.5 g of the N-mono and 1 g of the N,N-disubstitution derivatives
of ethanesulfonamide, to judge from the nitrogen analysis data.

<u>Analysis of N-propanol-2-methoxy-3-ethanesulfonamide</u>.

0.1202 g subs.: 5.99 ml 0.1 N. $H_2SO_4$ (Kjeldahl method); 0.1532 g subs.:
7.80 ml 0.1 N. $H_2SO_4$. Found %: N 6.97, 7.12. $C_6H_{15}SNO_4$. Calc. %: N 7.10.

<u>Analysis of N,N-di-(propanol-2-methoxy-3)-ethanesulfonamide</u>.

0.1490 g subs.: 5.70 ml 0.1 N $H_2SO_4$ (Kjeldahl method). Found %: N 5.35.
$C_{10}H_{23}SNO_6$. Calc. %: N 4.91.

The synthesized N-mono and N,N-disubstitution derivatives of ethanesulfona-
mide are yellow-brown oils with a faint odor, which are freely soluble in alcohol
and acetone. When fractionated in vacuum, the products begin to decompose in the
distilling flask at 127° (4 mm). The substances were not analyzed further owing
to the small quantities synthesized.

Experiments were also run under similar conditions on the reaction of glycidol
ethyl ether with ethanesulfonamide. We also secured a product that was freely sol-
uble in alcohol and acetone (sparingly soluble in petroleum ether). Repeated
efforts to isolate it in the pure state and identify it were unsuccessful. Nor
did we manage to isolate or identify the reaction products formed when the glycidol
methyl and ethyl ethers were reacted with benzenesulfonamide under the conditions
described.

<div align="center">SUMMARY</div>

    1. A study has been made of the reactions of the glycidol methyl and ethyl
ethers with acetamide, ethanesulfonamide, and benzenesulfonamide.

    2. The following products of these reactions: N-propanol-2-methoxy-3-
-acetamide, N,N-di-(propanol-2-methoxy-3)-acetamide, N-propanol-2-ethoxy-3-
-acetamide, and N,N-di-(propanol-2-ethoxy-3)-acetamide, have been isolated and
identified.

3.  It has been shown that it is much more difficult for the glycidol ethers to react with ethane- and benzenesulfonamides than with acetamide.

## LITERATURE CITED

[1]  F. G. Ponomarev and S. F. Popov, J. Gen. Chem. 20, 2064[*](1950).

[2]  A. A. Petrov, J. Gen. Chem. 10, 981 (1940).

[*]See Consultants Bureau English translation, p. 2131.

# THE SYNTHESIS OF SOME AMINOGUANIDINE DERIVATIVES

M. N. Shchukina and E. E. Mikhlina

A report [1] was published in the literature at the end of 1946 on the anti-tuberculosis activity _in vitro_ of some thiosemicarbazones. Several papers were published in 1947-1949 [2, 3, 4], dealing with investigations of a large number of thiosemicarbazones in experiments _in vivo_. According to the authors of these papers, the most active of these, p-acetaminobenzalthiosemicarbazone (the preparation Domagk Tb I 698) has been tested clinically and has been employed in treating some forms of tuberculosis.

We were interested in making a study of the antituberculosis activity of carbonyl derivatives of aminoguanidine. Structurally, the latter may be regarded as thiosemicarbazones in which the sulfur has been replaced by an amino group:

$$RCH=N-NHCNH_2 \qquad RCH=N-NHCNH_2$$
$$\underset{S}{\|} \qquad\qquad\qquad \underset{NH}{\|}$$

We synthesized the aminoguanyl derivatives of benzaldehyde, vanillin, and p-acetaminobenzaldehyde, as well as their N-butyl and N-octyl derivatives. The aminoguanidine required for synthesizing the aminoguanyl derivatives was prepared as its hydrochloride by reacting methylisothiourea with hydrazine sulfate [5]. The aminoguanyl derivatives of the foregoing aldehydes were synthesized by condensing aminoguanidine with aldehydes

The N-alkyl derivatives of the aminoguanyls were synthesized in two ways.

1. Reacting the hydriodides of S-methylthiosemicarbazones with alkyl amines:

$$RCH=NN=CNH_2 \cdot HI \qquad\qquad RCH=NNHCNH_2 \cdot HI + CH_3SH$$
$$\underset{SCH_3}{|} \quad\xrightarrow{R'NH_2}\quad \underset{NR'}{\|}$$
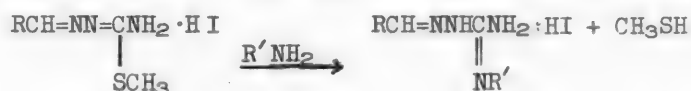
It was found that an alkyl amino group is substituted for the methylmercapto group in methylthiosemicarbazones when the constituents are boiled in alcohol for a long time. The lengthy heating causes partial tarring, which interferes with the isolation of the substance in the pure state.

2. Reacting an N-alkyl aminoguanidine with a carbonyl compound:

$$RCHO + NH_2NHCNH_2 \cdot HI \qquad\qquad RCH=NNHCNH_2 \cdot HI + H_2O$$
$$\underset{NR'}{\|} \quad\xrightarrow{\hspace{1cm}}\quad \underset{NR'}{\|}$$

$$(IV)$$

The N-alkyl aminoguanidines were synthesized as follows [6]:

$$NH_2NHCSNH_2 \qquad\qquad NH_2N=CNH_2 \cdot HI$$
$$\xrightarrow{CH_3I} \qquad \underset{SCH_3}{\|} \qquad \xrightarrow{+R'NH_2}$$
$$(I) \qquad\qquad\qquad (II)$$

$$NH_2NHCNH_2 \cdot HI$$
$$\xrightarrow{\hspace{2cm}} \underset{\overset{\displaystyle \|}{\underset{(III)}{NR}}}{} \qquad + CH_3SH .$$
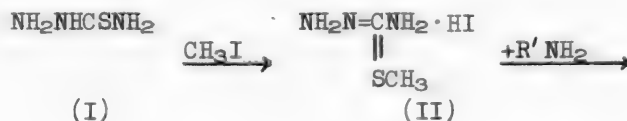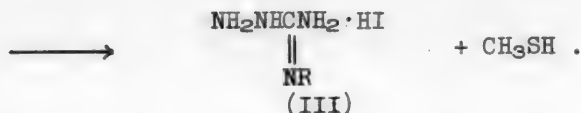
The thiosemicarbazide (I) was converted into S-methylisothiosemicarbazide hydriodide (II) by treating it with methyl iodide in alcohol. Reacting the latter with alkyl amines yielded hydriodides of N-alkyl aminoguanidines (III), which were condensed directly with carbonyl compounds. This yielded N-alkyl aminoguanidines (IV).

In contrast to the methylisothiosemicarbazones, replacing the alkyl amino group by a methylmercapto group was very easy in methylisothiosemicarbazide, requiring only 30 minutes of heating of molar quantities of the reagents in alcohol. The N-alkyl aminoguanyl hydriodides, secured as viscous oils, were converted into crystalline hydrochlorides by treating them with concentrated hydrochloric acid.

Tests of the antituberculosis activity of the synthesized preparations in vitro with a virulent strain of Mycobacterium tuberculosis (in the Division of Chemotherapy of the All-Union Research Institute of Pharmaceutical Chemistry) indicated that the $N^4$-octyl derivatives possessed greater bacteriostatic activity. The $N^4$-octyl-benzalaminoguanyl derivative was observed to retard growth completely in a 1:125,000 dilution, the corresponding dilution for the $N^4$-octyl-p--acetaminobenzalaminoguanyl being 1:32,000, the tuberculostatic activity being much less in the corresponding $N^4$-butyl substitution derivatives.

All these compounds are rather toxic, and, in view of their comparatively slight bacteriostatic activity, we consider that there is no prospect for them as antituberculosis preparations

## EXPERIMENTAL

3-Hydroxy-4-methoxybenzalaminoguanyl hydrochloride. An alcoholic solution of 3-hydroxy-4-methoxybenzaldehyde was treated with an aqueous solution of aminoguanidine hydrochloride (m.p. 163-164°). A few drops of hydrochloric acid were added to the transparent solution, and colorless crystals were thrown down at once; they had a m.p. of 215-216° after recrystallization from alcohol and ether. They were freely soluble in water and alcohol, slightly soluble in acetone, and insoluble in ether.

4.970 mg subs.: 2.852 mg AgCl; 4.139 mg subs.: 2.432 mg AgCl. Found %: Cl 14.69, 14.54. $C_9H_{13}O_2N_4Cl$. Calc. %: Cl 14.54.

The base was isolated by processing an aqueous solution of the hydrochloride with soda. M.p. 135° (with decomposition).

p-Acetaminobenzalaminoguanyl hydrochloride. This was prepared similarly. Snow-white crystals, slightly soluble in alcohol, readily soluble in water. M.p. 250-251.5°.

5.255 mg subs.: 2.903 mg AgCl; 4.750 mg subs.: 2.648 mg AgCl. Found %: Cl 13.67, 13.79. $C_{10}H_{14}ON_5Cl$. Calc. %: Cl 13.93.

The bases had a m.p. of 222° (with decomposition). The m p. of benzalaminoguanyl hydrochloride is given in the literature as 50° [7].

158

3-Hydroxy-4-methoxybenzal-$N^4$-butylaminoguanyl hydrochloride. a) 1 g of 3-hydroxy-4-methoxy-benzal-5-methylisothiosemicarbazone was boiled for 18 hours in 10 ml of absolute alcohol with 22 g of n-butylamine. The alcohol was evaporated in vacuo, and the residual oil was triturated with dilute hydrochloric acid. The resulting brown crystals were refined by repeated recrystallization from alcohol containing activated charcoal. M.p. 198-199°.

b) 2 g of thiosemicarbazide and 3.14 g of methyl iodide were heated in 15 ml of absolute alcohol until all the thiosemicarbazide dissolved, and 1.6 g of n-butylamine was added to the resulting alcoholic solution of 5-methyliso-thiosemicarbazide hydriodide. The solution was boiled for 30 minutes. Then the alcohol was evaporated in vacuo, and the remaining N-butylaminoguanidine, a thick oil, was treated with a solution of 3.25 g of vanillin in 10 ml of alcohol and a few drops of hydrochloric acid. The mixture was boiled for an hour, the alcohol driven off in vacuo, and the oil thoroughly triturated with dilute hydrochloric acid. The yellowish precipitate was recrystallized twice from alcohol. M.p. 200-201°. The product was the same as that prepared by the previous method.*

p-Acetaminobenzal-$N^4$-butylaminoguanyl hydriodide. 1 g of thiosemicarbazide, 1.57 g of methyl iodide, 0.85 g of n-butylamine, and 1.79 g of p-acetaminobenzaldehyde were processed in the same sequence of operations as that described in Test (b) for the $N^4$-butylaminoguanyl derivative of vanillin. The crystals secured after repeatedly treating the oily reaction product with hydrochloric acid were not the expected hydrochloride, but p-acetaminobenzaldehyde-$N^4$-butylaminoguanyl hydriodide. The latter was purified by recrystallization from water with activated charcoal; a light-yellow substance with a m.p. of 223-225°.

3.294 mg. subs.: 0.516 ml $N_2$ (29°, 721 mm). Found %: N 16.78. $C_{14}H_{22}N_5OI$. Calc. %: N 17.23.

Benzal-$N^4$-butylaminoguanyl hydrochloride. These snow-white crystals were secured after double recrystallization from a small amount of alcohol. M.p. 210.5-212°.

3.926 mg subs.: 0.784 ml $N_2$ (26.5°, 724 mm). Found %: N 21.67. $C_{12}H_{19}N_4Cl$. Calc. %: N 21.97.

Benzal-$N^4$-octylaminoguanyl hydrochloride. These snow-white crystals were secured from alcohol containing ether. M.p. 176-177°.

3.000 mg subs.: 7.544 mg $CO_2$; 2.560 mg $H_2O$; 3.141 mg subs.: 0.526 ml $N_2$ (30.0°, 724 mm). Found %: C 62.43; H 8.68; N 17.94. $C_{16}H_{27}N_4Cl$. Calc. %: C 61.99; H 8.69; N 18.03.

p-Acetaminobenzal-$N^4$-octylaminoguanyl hydrochloride. This was synthesized as yellow crystals by recrystallization from water containing activated charcoal, followed by recrystallization from alcohol. M.p. 211-213°. Freely soluble in alcohol and acetone, less so in water, and insoluble in ether.

3.195 mg subs.: 0.537 ml $N_2$ (22°, 730 mm); 3.225 mg subs.: 0.544 ml $N_2$ (22°, 732 mm). Found %: N 18.70, 18.93. $C_{18}H_{30}ON_5Cl$. Calc. %: N 19.03.

## SUMMARY

Several benzalguanyl substitution derivatives and their $N^4$-alkyl derivatives have been synthesized. These compounds possess antituberculosis activity, but are toxic.

3.752 mg subs.: 7.188 mg $CO_2$; 2.339 mg $H_2O$; 3.426 mg subs.: 6.548 mg $CO_2$; 2.090 mg $H_2O$; 3.301 mg subs.: 0.577 ml $N_2$ (29.5°, 720.5 mm); 5.300 mg subs.: 2.618 mg AgCl. Found %: C 52.32, 52.12; H 6.97, 6.82; N 18.69; Cl 12.22. $C_{13}H_{21}N_4O_2Cl$. Computed %: C 51.95; H 6.98; N 18.63; Cl 11.83.

LITERATURE CITED

[1]  Domagk, Naturwissenschaften, 33, 315 (1946).

[2]  C. Moncorps, K. W. Kalcoff, Med. Klinik (Munich), 42, 812 (1947).

[3]  Domagk, Beitr. Klinik Tuberk. 101, 365 (1948).

[4]  E. Hoggarth, Brit. J. Pharmacol.1, 4, 3, 248 (1949).

[5]  Organic Synthesis, No. 26, p. 9.

[6]  G. Kristen, G. Smith, J. Am. Chem. Soc., 58, 800 (1936).

[7]  Thiele, Ann., 270, 36 (1892).

# MIXED SULFIDES WITH $C_{11}$ - $C_{20}$ CARBON ATOMS

## AND THEIR FUNDAMENTAL CONSTANTS

I. M. Tits-Skvortsova, S. Ya. Levina,

A. I. Leonova and T. A. Danilova

We are the first to have synthesized the hitherto undescribed mixed sulfides whose synthesis and constants are set forth in this report.

These sulfides have been produced by the general method first proposed by F. Kruger [1] for synthesizing mixed sulfides, viz.: reacting metallic derivatives of the thiols with the appropriate halides as follows:

$$R-S-Me + R_1Hal \rightarrow R-S-R_1 + MeHal.$$

The usual procedure employed to synthesize these sulfides was as follows: equimolecular quantities of the thiol, a caustic alkali (caustic potash or soda), and an alkyl halide were used. The apparatus in which the synthesis was carried out consisted of a round-bottomed flask fitted with a dropping funnel and a reflux condenser. The caustic alkali was dissolved by heating it on a water bath with 1.5-2 mols of ethyl alcohol or methanol. Then the thiol was added a drop at a time to the alcoholic solution of the alkali without interrupting the heating. When all the thiol had been added, the reaction mass was heated to 60-70 for 30 minutes. Then the alkyl halide was added drop by drop, the bath being kept at that same temperature. This usually caused a white precipitate of the metal halide to settle out at once. When all the alkyl halide had been added, the heating of the reaction mixture to 60-70° was continued for another 1.5-2 hours. The sulfide settled out as an oily layer. After the mixture had cooled, water was added to the flask, causing the metal halide to dissolve. The sulfide was extracted with ether, the ether extract being washed with a 10% alkali solution to eliminate the unreacted thiol and with water until its reaction was neutral, after which it was dried with calcium chloride. The ether was then driven off, and the synthesized sulfide fractionated in vacuo.

In calculating the molar refractions we took the atomic refraction of sulfidic sulfur to be 7.97, in conformity with the findings of T. S. Price and D. F. Twiss [2]. The parallel determinations of carbon, hydrogen, and sulfur were made by the procedure elaborated by M. O. Korshun and his associates [3,4].

1. Phenyl decyl sulfide was produced by reacting potassium thiophenolate with decyl bromide. The yield was 84.4% of the theoretical.

The thiophenol was prepared by the method described in Syntheses of organic preparations [5] and had the following constants: b.p. 68 (22 mm); $n_D^{20}$ 1.5888; $d_4^{20}$ 1.0780. The figures given in the literature are: b.p. 77 (30 mm); $n_D^{23.2}$ 1.58613; $d_4^{23.2}$ 1.0739[6].

The decyl bromide was prepared from decyl alcohol by reacting it with bromine and phosphorus; it had a b.p. of 97-98° (5 mm); $n_D^{20}$ 1.4550; $d_4^{20}$ 1.0689.

Figures in the literature: b.p. 104-104.5° (8 mm); $n_D^{20}$ 1.45504; $d_4^{20}$ 1.0683 [7].

Constants of phenyl decyl sulfide: b.p. 170-171° (5 mm); m.p. 21°; $n_D^{24}$ 1.5213; $d_4^{24}$ 0.9341; $MR_D$ 81.47; Calc. 80.46.

3.775 mg subs.: 10.620 mg $CO_2$; 3.420 mg $H_2O$. 3.920 mg subs.: 10.800 mg $CO_2$; 3.600 mg $H_2O$. Found %: C 76.84, 76.89; H 10.15, 10.28. $C_{16}H_{26}S$. Calc. %: C 76.8; H 10.4.

2. Phenyl cyclopentyl sulfide was synthesized from potassium thiophenolate and cyclopentyl bromide, the yield being 65%.

The cyclopentyl bromide, prepared by saturating cyclopentanol with gaseous hydrogen bromide [8], had a b.p. of 135° (746 mm); $n_D^{20}$ 1.4890; $d_4^{20}$ 1.3863.

The figures given in the literature for cyclopentyl bromide: b.p. 136-138°; $d^4$ 1.370 [8]; b.p. 136-138°; $d_0^0$ 1.380 [10]; b.p. 137-139°; $n_D^{19}$ 1.4875; $d_{19}^{19}$ 1.400 [11].

Constants of phenyl cyclopentyl sulfide: b.p. 139.5° (13 mm); $n_D^{20}$ 1.5740; $d_4^{20}$ 1.0571; $MR_D$ 55.62; Calc. 55.17.

5.040 mg subs.: 13.645 mg $CO_2$; 3.525 mg $H_2O$. 5.390 mg subs.: 14.645 mg $CO_2$; 3.765 mg $H_2O$. Found %: C 73.98, 74.15; H 7.82, 7.89. $C_{11}H_{14}S$. Calc. %: C 74.08; H 7.92.

3. Cyclohexyl decyl sulfide was synthesized by reacting a sodium derivative of cyclopentanol with decyl bromide, the yield being 62%.

Cyclohexanethiol was prepared by reacting cyclohexylmagnesium bromide with sulfur [12]. Constants of cyclohexanethiol: b.p. 90-91° (100 mm); $n_D^{20}$ 1.4911; $d_4^{20}$ 0.9584.

Figures in the literature for cyclohexanethiol: b.p. 90° (100 mm); $n_D^{20}$ 1.4933; $d_4^{20}$ 0.9486 [13].

Constants of cyclohexyl decyl sulfide: b.p. 164-165° (2 mm); $n_D^{20}$ 1.4820; $d_4^{20}$ 0.8846; $MR_D$ 82.48; Calc. 81.86.

6.000 mg subs.: 16.520 mg $CO_2$; 6.818 mg $H_2O$. 3.960 mg subs.: 10.885 mg $CO_2$; 4.450 mg $H_2O$. 5.990 mg subs.: 2.270 mg $SO_4$. 6.460 mg subs.: 2.450 mg $SO_4$. Found %: C 75.14, 75.02; H 12.71, 12.57. S 12.65, 12.66. $C_{16}H_{32}S$. Calc. %: C 75.0; H 12.5; S 12.5.

An attempt to synthesize cyclohexyl decyl sulfide by reacting cyclohexyl bromide with sodium decyl mercaptide was less successful. The sulfide yield was 17%, due to a side reaction in which the influence of the alkali caused the formation of cyclohexene from the cyclohexyl bromide.

4. Cyclopentyl decyl sulfide was synthesized by reacting the potassium mercaptide of cyclopentanethiol with decyl bromide.

Cyclopentanethiol was prepared by reacting potassium hydrosulfide with cyclopentyl bromide [14]. The constants of the cyclopentanethiol were: b.p. 130° (746 mm); $n_D^{20}$ 1.4882; $d_4^{20}$ 0.9485. The literature gives the b.p. of cyclopentanethiol as 131.5-132° [14], no other constants being cited.

Cyclopentyl decyl sulfide was synthesized in the usual manner. The yield was 72% of the theoretical.

B.p. 158° (2 mm); $n_D^{20}$ 1.4786; $d_4^{20}$ 0.8833; $MR_D$ 77.72; Calc. 77.24.

6.060 mg subs.: 16.505 mg $CO_2$; 6.800 mg $H_2O$. 2.410 mg $SO_4$. 6.480 mg subs.: 17.625 mg $CO_2$; 7.230 mg $H_2O$; 3.220 mg $SO_4$. Found %: C 74.35, 74.25; H 12.55, 12.49; S 13.28, 13.18. $C_{15}H_{30}S$. Calc. %: C 74.29; H 12.48; S 13.23.

5. Cyclohexyl cyclopentyl sulfide was synthesized by reacting the potassium mercaptide of cyclohexanethiol with cyclopentyl bromide. The yield was 67% of the theoretical.

B.p. 119-120° (3 mm); $n_D^{20}$ 1.5118; $d_4^{20}$ 0.9692; $MR_D$ 56.90; Calc. 56.57.

6.290 mg subs.: 16.520 mg $CO_2$; 6.250 mg $H_2O$; 3.270 mg $SO_4$. 5.100 mg subs.: 13.370 mg $CO_2$; 5.080 mg $H_2O$; 2.650 mg $SO_4$. Found %: C 71.67, 71.56; H 11.12, 11.15; S 17.35, 17.34. $C_{11}H_{20}S$. Calc. %: C 71.73; H 10.87; S 17.38..

6. α-Naphthyl decyl sulfide was synthesized from potassium α-thionaphtholate and decyl bromide.

The α-thionaphthol was prepared by reducing α-naphthalene monosulfonic chloride with zinc dust and hydrochloric acid [15]. The constants of the resultant α-thionaphthol were: b.p. 142-142.5° (7 mm); $n_D^{20}$ 1.6802; $d_4^{20}$ 1.1607.

Figures in the literature for α-thionaphthol: b.p. 144.8° (10.3 mm) [15]; b.p. 152.5-153.5° (15 mm); $d_4^{20}$ 1.1549 [16].

In synthesizing α-naphthyl decyl sulfide we departed from the standard procedure by heating the reaction mixture on a glycerol bath at 120-130° instead of carrying it out at 60-70° as is customary. This was done because F. Kraft and R. Schonherr [16], who synthesized α-naphthyl ethyl sulfide, recommend that the reaction be carried out at higher temperatures when α-thionaphthol is used. The yield of α-naphthyl decyl sulfide was 72% of the theoretical.

B.p. 234-235° (7-8 mm); $n_D^{20}$ 1.5714; $d_4^{20}$ 0.9893; $MR_D$ 99.64; Calc. 95.80.

4.800 mg subs.: 14.060 mg $CO_2$; 4.090 mg $H_2O$; 1.535 mg $SO_4$. 4.980 mg subs.: 14.585 mg $CO_2$; 4.240 mg $H_2O$; 1.595 mg $SO_4$. Found %: C 79.94, 79.92; H 9.54, 9.53; S 10.67, 10.89. $C_{20}H_{28}S$. Calc. %: C 80.0; H 9.33; S 10.66.

7. α-Naphthyl cyclohexyl sulfide was synthesized from sodium α-thionaphtholate and cyclohexyl bromide.

The cyclohexyl bromide was synthesized by saturating cyclohexanol with gaseous hydrogen bromide [17]. The constants of the synthesized cyclohexyl bromide were: b.p. 163-164° (760 mm); $n_D^{20}$ 1.4950; $d_4^{20}$ 1.3357.

Figures in the literature: b.p. 163-165.5°; $d_0^0$ 1.3604 [18]; b.p. 163-166.5° (760 mm); $n_D^{14.6}$ 1.49564; $d_4^{14.6}$ 1.3264 [19].

The conditions employed in synthesizing α-naphthyl cyclohexyl sulfide were the same as those used in synthesizing the preceding preparation, i.e., heating on a glycerine bath to 120°. The yield of α-naphthyl cyclohexyl sulfide was 31.4% of the theoretical. This low yield was due to a side reaction in which cyclohexene was formed, 35% of the initial cyclohexyl bromide being converted into cyclohexene.

The constants of the synthesized α-naphthyl cyclohexyl sulfide were: b.p. 201-202° (7 mm); $n_D^{20}$ 1.6306; $d_4^{20}$ 1.0953; $MR_D$ 78.64; Calc. 75.12.

5.650 mg subs.: 16.435 mg $CO_2$; 3.740 mg $H_2O$; 2.230 mg $SO_4$. 6.030 mg subs.: 17.535 mg $CO_2$; 4.070 mg $H_2O$; 2.400 mg $SO_4$. Found %: C 79.39, 79.36; H 7.47, 7.55; S 13.18, 13.28. $C_{16}H_{18}S$. Calc. %: C 79.34; H 7.43; S 13.22.

163

8. β-Tetralyl cyclohexyl sulfide was synthesized from the sodium derivative of β-thiotetralol and cyclohexyl chloride.

The β-thiotetralol was prepared by reducing β-tetralin sulfochloride with zinc dust and hydrochloric acid [20].

Constants of β-thiotetralol: b.p. 151-151.5° (15 mm); $n_D^{20}$ 1.5972; $d_4^{20}$ 1.0884.

Figures in the literature: b.p. 146-148° (14 mm) [20].

The cyclohexyl chloride (a ready preparation) had a b.p. of 141.5-142.5° (749 mm); $n_D^{20}$ 1.4610; $d_4^{20}$ 1.0030. The figures given in the literature for cyclohexyl chloride are: b.p. 141° (760 mm); $n_D^{20}$ 1.46264; $d_4^{20}$ 1.0000 [9].

The β-tetralyl cyclohexyl sulfide was synthesized by heating the reaction mixture to 120° on a glycerin bath. The yield was 34.9% of the theoretical. The low sulfide yield is attributable to a side reaction in which the alcoholic alkali converted the cyclohexyl chloride into cyclohexene.

Attempts to synthesize the tetralyl cyclohexyl sulfide from cyclohexyl bromide produced an even lower yield of the sulfide. Lowering the reaction temperature likewise lowered the yield.

Constants of the synthesized β-tetralyl cyclohexyl sulfide: b.p. 187.5-188.5° (3 mm); $n_D^{20}$ 1.5800; $d_4^{20}$ 1.0543; $MR_D$ 77.65; Calc. 75.92.

5.735 mg subs.: 16.450 mg $CO_2$; 4.580 mg $H_2O$; 2.240 mg $SO_4$. 6.090 mg subs.: 17.425 mg $CO_2$; 4.875 mg $H_2O$; 2.360 mg $SO_4$. Found %: C 78.28, 78.11; H 8.95, 8.96; S 13.03, 12.94. $C_{16}H_{22}S$. Calc. %: C 77.99; H 9.00; S 13.01.

## SUMMARY

The following mixed sulfides have been synthesized and described for the first time by reacting aliphatic and naphthenic halogen derivatives with metallic derivatives of aliphatic, aromatic, and naphthenic thiols: phenyl decyl sulfide, phenyl cyclopentyl sulfide, cyclohexyl decyl sulfide, cyclopentyldecyl sulfide, cyclohexyl cyclopentyl sulfide, α-naphthyl decyl sulfide, α-naphthyl cyclohexyl sulfide, and β-tetralyl cyclohexyl sulfide.

The yields were satisfactory (ranging from 62 to 84%) except when the halide used was a cyclohexyl halide. Then the yields dropped to 30-34% owing to a side reaction in which cyclohexene was formed.

## LITERATURE CITED

[1]  F. Kruger, J. prak. Chem., (2), 14, 206 (1876).

[2]  T. S. Price, D. F. Twiss, J. Chem. Soc., 101, 1264 (1912).

[3]  M. O. Korshun and N. E. Gelman. New methods of ultimate microanalysis, p. 51. (1949).

[4]  M. O. Korshun and N. S. Sheveleva, Proc. USSR Acad. Sci. 60, 63 (1948).

[5]  Syntheses of organic preparations (Russ. ed.), v. I, 381 (1949).

[6]  F. Eisenlohr, Ber., 44, 3207 (1911).

[7]  G. Komppa, J. Talvitie, J. prak. Chem., 135, 193 (1932).

[8]  J. Wislicenus, W. Hentschel, Ann., 276, 324 (1893).

[9]  E. Krause, R. Pohland, Ber., 57, 534 (1924).

[10] N. Demyanov and M. Lushnikov, J. Russ. Chem. Soc. 35, 31 (1903).

[11] N. Demyanov, Ber., 40, 4960 (1907).

[12] A. Mailhe, M. Murat, Bull. Soc. Chem. (4), 7, 288 (1910).

[13] M. W. Farlow, F. S. Signaigo, C. A. 1946, 5759.

[14] J. Loevenich, H. Utsch, P. Moldrick, E. Schaefer, Ber., 62, 3084 (1929).

[15] Ed. Bourgeois, Rec. trav. chim., 18, 441 (1899).

[16] F. Kraft, R. Schonherr, Ber., 22, 822 (1889).

[17] J. R. Ruhoff, R. E. Burnett, E. E. Reid, J. Am. Soc., 56, 2784 (1934).

[18] A. Favorsky and I. Borgman, Ber., 40, 4864 (1907).

[19] E. C. Fortey, J. Chem. Soc., 73, 947 (1898).

[20] G. Schroeter, Ann., 426, 85, 117 (1922).

# SYNTHESIS OF THE DISACCHARIDES

## VI. SYNTHESIS OF GLUCOSIDO-2-GALACTOSE

### A. M. Gakhokidze and N. D. Kutidze

In our previous research the following disaccharides have been synthesized: glucosido-2-glucose [1], galactosido-2-galactose [2], galactosido-2-glucose [3], glucosido-3-glucose, and galactosido-3-glucose [5]. In the present paper we shall describe the synthesis of glucosido-2-galactose.

The initial substances used in this synthesis were 2,3,4,6-tetraacetylglucose (I) and 1,3,4,6-tetraacetylgalactose (IV). β-2,3,4,6-Tetraacetylglucose was synthesized from glucose via the pentaacetate and acetobromoglucose [6]. The 1,3,4,6-tetraacetylgalactose was synthesized from pentaacetylgalactose [7], which was converted by the action of phosphorus pentachloride into 1-chloro-2-(trichloroacetyl)--3,4,6-triacetylgalactose (II), saponification of the latter compound with ammonia in ether solution readily yielding 1-chloro-3,4,6-triacetylgalactose (III). Reacting 1-chloro-3,4,6-triacetylgalactose with silver acetate yielded 1,3,4,6-tetraacetylgalactose (IV).
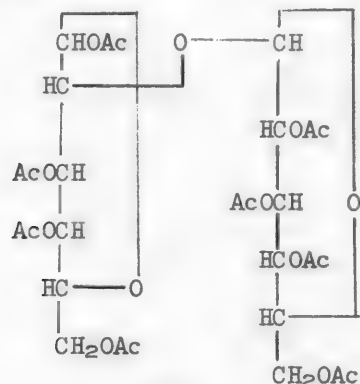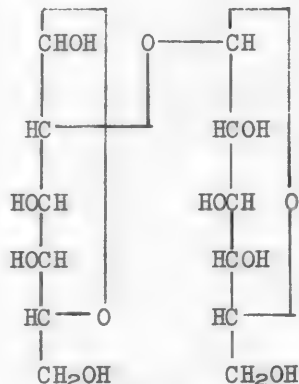
| (I) | (II) | (III) | (IV) |
|-----|------|-------|------|
| HOCH | CHCl | CHCl | CHOAc |
| HCOAc | HCOCOCCl₃ | HCOH | HCOH |
| AcOCH  O | AcOCH  O | AcOCH  O | AcOCH  O |
| HCOAc | AcOCH | AcOCH | AcOCH |
| HC | HC | HC | HC |
| CH₂OAc | CH₂OAc | CH₂OAc | CH₂OAc |
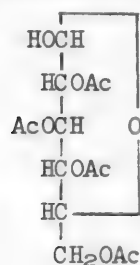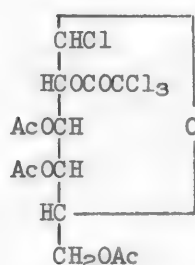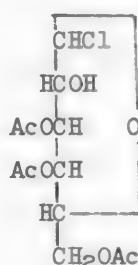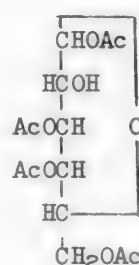
Condensing β-2,3,4,6-tetraacetylglucose with 1,3,4,6-tetraacetylgalactose yielded the octaacetate of glucosido-2-galactose (V), which was converted into glucosido-2-galactose (VI).
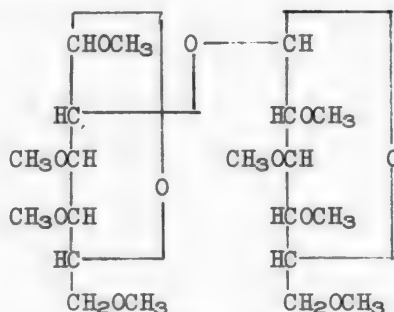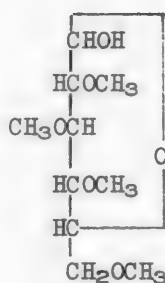
(V) and (VI) structural formulas.

(V)          (VI)

The disaccharide was identified as its hydrazone and its bionic acid. It reduces Fehling's solution. Splitting a hydrogen atom from the reducing part of the disaccharide yielded glucosidopentose, which does not reduce Fehling's solution or react with phenylhydrazine.
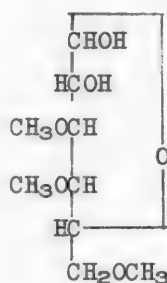
The positions of the oxygen bridges were determined by methylation, hydrolysis and oxidation. Hydrolysis of the completely methylated disaccharide (VII) yielded 2,3,4,6-tetramethylglucose (VIII) and 3,4,6-trimethylgalactose (IX). 2,3,4,6-Tetramethylglucose was identified as its anilide, and the 3,4,6-trimethylgalactose via its $\delta$-lactone (X). The production of 2,3,4,6-tetramethylglucose and of the $\delta$-lactone is evidence of the pyranose structure of the two monoses comprising the disaccharide we had synthesized.
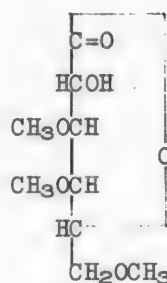
$$
\begin{array}{ll}
CHOCH_3 & O\text{----}CH \\
HC & HCOCH_3 \\
CH_3OCH & CH_3OCH \quad O \\
CH_3OCH & HCOCH_3 \\
HC & HC \\
CH_2OCH_3 & CH_2OCH_3
\end{array}
$$

(VII)

$$
\begin{array}{lll}
CHOH & CHOH & C=O \\
HCOCH_3 & HCOH & HCOH \\
CH_3OCH & CH_3OCH & CH_3OCH \\
HCOCH_3 \quad O & CH_3OCH \quad O & CH_3OCH \quad O \\
HC & HC & HC \\
CH_2OCH_3 & CH_2OCH_3 & CH_2OCH_3
\end{array}
$$

(VIII)          (IX)          (X)

These findings, plus the course of the synthesis itself, indicate that the disaccharide has the structure of (1,5)-glucosido-2-(1,5)-galactose (VI).

### EXPERIMENTAL

1. 1-Chloro-2-(trichloroacetyl)-3,4,6-triacetylgalactose. A mixture of 117.0 g of pentaacetylgalactose and 200 g of phosphorus pentachloride was placed in a flask with a ground-glass-fitted reflux condenser terminating in a calcium chloride tube and heated on a water bath for 3 hours. When the reaction was over (test for evolution of hydrogen chloride), the reaction solution was distilled at reduced pressure (2 mm). The oily distillate was dissolved in 10 ml of amyl alcohol; chilling the alcohol threw down a precipitate that was filtered out and washed with cold anhydrous ether. The yield was 63.1 g, or 46% of the theoretical.

1-Chloro-2-(trichloroacetyl)-3,4,6-triacetylgalactose is freely soluble in benzene, chloroform, acetone, ether, methanol, and ethyl alcohol, reduces Fehling's solution, and throws down a precipitate with silver nitrate.

168

The melting point of the pure product was 150-156°; $\alpha_D^{20}$ 10.4° (in benzene, C = 2.71). 0.0964 g subs.: 0.1194 g AgCl. Found %: Cl 30.61. $C_{14}H_{18}O_9Cl_4$. Calc. %: Cl 30.21.

2. 1-Chloro-3,4,6-triacetylgalactose. 58 g of 1-chloro-2-(trichloroacetyl)--3,4,6-triacetylgalactose was dissolved in 400 ml of anhydrous ether that had been saturated with anhydrous ammonia at 0°. Then the reaction solution was kept at room temperature for 3 hours and chilled strongly, causing the precipitation of flocs of the ammonium salt. The solution was filtered and then evaporated to dryness, the 1-chloro-3,4,6-triacetylgalactose being extracted from the residue with ethyl acetate. After the ethyl acetate had been driven off, the resultant crystals were recrystallized from ethyl alcohol. The yield was 23.7 g, or 59% of the theoretical.

M.p. 159-167°; $\alpha_D^{20}$ + 29.10° (in ethyl acetate, C = 3.40).

1-Chloro-3,4,6-triacetylgalactose is freely soluble in ether, acetone, chloroform, and ethyl alcohol.

0.1013 g subs.: 0.0435 g AgCl; 0.1519 g subs.: 0.0666 g AgCl. Found %: Cl 10.64, 10.77. $C_{12}H_{17}O_8Cl$. Calc. %: Cl 10.94.

The 1-chloro-3,4,6-triacetylgalactose was also identified via α-tetraacetylgalactose [m.p. 95-96°; $\alpha_D^{20}$ + 106° (in chloroform)] and 1,2-dichloro-3,4,6-triacetylgalactose [m.p. 99-101°; $\alpha_D^{20}$ + 37.4° (in ethyl alcohol)].

3. 1,3,4,6-Tetraacetylgalactose. 16.2 g of 1-chloro-3,4,6-triacetylgalactose was dissolved in 300 ml of anhydrous ether. 16.6 g of silver acetate was added to the resulting solution, and the whole was agitated at room temperature for 2 hours (until a solution sample no longer exhibited the presence of any halogens). After the silver salts had been filtered out, the ether was evaporated to dryness, the reaction product being extracted from the residue with chloroform at first and then with ether. The chloroform and ether extracts were combined, desiccated, and evaporated to dryness. The substance was refined by recrystallizing it from ethyl alcohol. The yield was 12.9 g, or 74% of the theoretical. The melting point of the pure product was 128°; $\alpha_D^{20}$ + 11.70° (in ethyl alcohol, C = 2.00).

1,3,4,6-Tetraacetylgalactose is freely soluble in chloroform, ether, acetone, ethyl alcohol, and pyridine.

0.1234 g subs.: 0.2197 g $CO_2$; 0.0781 g $H_2O$; 0.0849 g subs.: 0.1564 g $CO_2$; 0.0488 g $H_2O$; 0.1810 g subs.: 21.2 ml 0.1 N NaOH. Found %: C 48.15, 48.52; H 6.40, 6.31; $COCH_3$ 49.17. $C_{14}H_{20}O_{10}$. Calc. %: C 48.28; H 5.71; $COCH_3$ 49.40.

4. Condensing 2,3,4,6-tetraacetylglucose with 1,3,4,6-tetraacetylgalactose. A mixture of 12.5 g of 2,3,4,6-tetraacetylglucose and 12.5 g of 1,3,4,6-tetraacetylgalactose was dissolved in 350 ml of anhydrous chloroform. 6 g of fused zinc chloride was added, and the solution was agitated for 5 hours. The solution was filtered, 15 g of phosphoric anhydride was added, and agitation was continued. Five hours later the chloroform layer was filtered out, desiccated, and evaporated to dryness, the residue being recrystallized twice from ethyl alcohol. The yield was 22 g, or 81% of the theoretical. The melting point of the pure product was 179°.

0.1181 g subs.: 0.1841 g $CO_2$; 0.0567 g $H_2O$. 0.1701 g subs.: 0.2634 g $CO_2$, 0.0871 g $H_2O$; 0.1561 g subs.: 18.7 ml 0.1N Na OH; 0.2107 g subs.: 25 ml 0.1 N NaOH. Found %: C 48.95, 49.26; H 5.34, 5.70; $COCH_3$ 50.52,

50.39.  $C_{28}H_{38}O_{19}$.  Calc. %:  C 49.56;  H 5.60;  $COCH_3$ 50.64.

5.  β-(1,5)-Glucosido-2-(1,5)-galactose.  20 g of β-(1,5)-glucosido-2--(1,5)-galactose octaacetate was dissolved in 150 ml of anhydrous chloroform, the solution was chilled, and 0.7 g of sodium dissolved in 100 ml of absolute methanol was added.  The reaction mixture was agitated for 2 hours, a syrupy substance gradually settling out of the solution;  then 50 ml of water was added, and agitation was continued.  The mixture was neutralized with dilute acetic acid, and the chloroform layer was separated from the aqueous-alcoholic layer, which was evaporated in vacuo to a thick syrup.  The residue was stirred with 300 ml of methanol and 200 ml of acetone.  The solution was filtered 15 minutes later and then evaporated to dryness.  The residual substance was dissolved in the minimum quantity of water and mixed with 40 ml of glacial acetic acid, which threw crystals of the disaccharide down from the solution.  The yield was 7 g, or 81% of the theoretical:

M.p. 171-172°;  $\underline{1}$ = 0.5;  C = 0.3;  α + 6.4°;  $\alpha \frac{2}{D}$ + 42.6° (in water).

0.5101 g subs.:  0.7121 g $CO_2$;  0.2581 g $H_2O$;  0.6034 g subs.:  0.9242 g $CO_2$;  0.3601 g $H_2O$.  Found %:  C 42.60, 42.78;  H 5.82, 6.33.  $C_{12}H_{22}O_{11}$. Calc. %:  C 42.11;  H 6.43.

The melting point of the glucosido-2-galactose phenylhydrazone was 181°.

0.1134 g subs.:  5.9 ml $N_2$ (15°, 732 mm);  0.1891 g subs.:  9.9 ml $N_2$ (15°, 732 mm).  Found %:  N 6.13, 5.95.  $C_{18}H_{28}O_{10}N_2$.  Calc. %:  N 6.49.

6.  Oxidizing β-(1,5)-glucosido-2-(1,5)-galactose and hydrolysis of the resultant bionic acid.  5 g of β-(1,5)-glucosido-2-(1,5)-galactose was dissolved in 250 ml of bromine water, and the resultant solution was agitated and then exposed to light.  Then the solution was neutralized with calcium carbonate, filtered, and evaporated to minimum volume.  When absolute ethyl alcohol was slowly added to the thickened solution, flocs of the calcium salt of glucosido-2-galactonic acid settled out.  The salt was filtered out and recrystallized from water.

0.0721 g subs.:  0.0056 g CaO;  0.0854 g subs.:  0.0067 g CaO.  Found %: Ca 5.68, 5.74.  $(C_{12}H_{21}O_{12})_2Ca$.  Calc. %:  Ca 5.31.

When the calcium salt of glucosido-2-galactonic acid was decomposed with the calculated quantity of oxalic acid and the calcium salts had been filtered out of the solution, the resultant acid was hydrolyzed with a 5% solution of sulfuric acid.  The solution was neutralized with calcium carbonate and filtered, the filtrate being evaporated to minimum volume.  When absolute ethyl alcohol was slowly added to the thickened solution, flocs of calcium galactonate settled out;  the precipitate was filtered out and crystallized from water.

0.1101 g subs.:  0.0145 g CaO.  Found %:  Ca 9.39.  $(C_8H_{11}O_7)_2Ca$.  Calc. %:  Ca 9.30.

After the calcium galactonate had been filtered out, the filtrate was boiled with phenylhydrazine and acetic acid.  As the solution cooled, crystals with a m.p. of 205-207° settled out.  The mixed melting point with glucosazone exhibited no depression.

7.  Oxidation of the calcium salt of glucosido-2-galactonic acid.  5.5 g of the calcium salt of glucosido-2-galactonic acid was dissolved in 100 ml of water, and 1 g of barium acetate in 100 ml of water and 0.5 g of ferric sulfate in 15 ml of water were added to the solution.  The solution was then heated to 70°, and

30 ml of 30% perhydrol was gradually added, with frequent stirring. Then the reaction mixture was allowed to stand at room temperature for 3 hours, with frequent stirring, after which 25 ml more of the perhydrol was added to the solution. The solution warmed up slightly toward the end. The solution was filtered through charcoal and then evaporated to a thick syrup at reduced pressure. The residual glucosido-lycoside did not reduce Fehling's solution nor did it react with phenylhydrazine.

The product crystallized after standing for a long time with glacial acetic acid. The pure product had a m.p. of 139-141°; $\alpha_D^{20} + 5.4°$ (in water, C = 0.8).

0.1289 g subs.: 0.2013 g $CO_2$; 0.0812 g $H_2O$; 0.01 g subs.: 0.1 g camphor: $\Delta t$ 12.7°; 0.01 g subs.: 0.1 g camphor: $\Delta t$ 12.5° Found %: C 42.66; H 7.01; M 316, 319. $C_{11}H_{20}O_{10}$. Calc.: C 42.30; H 6.45; M 312.

The melting point of the acetylated product was 147-149°.

0.1137 g subs.: 13.1 ml 0.1 N Solution NaOH; 0.1783 g subs.: 20.4 ml 0.1 N. solution NaOH. Found %: $COCH_3$ 49.71, 49.30. $C_{25}H_{34}O_{17}$. Calc. %: $COCH_3$ 49.61.

8. Methylating glucosido-2-galactose. 8.4 g of glucosido-2-galactose was dissolved in 25 ml of water, and dimethyl sulfate and a 25% solution of sodium hydroxide were gradually added to the resulting solution at 40-60°, a total of 40 g of dimethyl sulfate being added. The alkali was added until the reaction of the solution was weakly alkaline. Toward the end the reaction mixture was heated to 100°, and the reaction product was extracted with chloroform. After the chloroform had been evaporated, the remaining syrup was remethylated, this time using 30 g of methyl iodide with 12 g of silver carbonate. The methylated glucosido-2-galactose was extracted with chloroform and distilled in a 2-mm vacuum after the chloroform had been driven off: $n_D^{20}$ 1.4712; $\alpha_D^{20} - 22.7°$ (in chloroform, C = 0.5). The yield was 15.8 g, or 57% of the theoretical.

0.1001 g subs.: 0.4125 g AgI; 0.1209 g subs.: 0.4927 g AgI. Found %: $OCH_3$ 55.02, 54.72. $C_{20}H_{38}O_{11}$. Calc. %: $OCH_3$ 54.65.

9. Hydrolysis of the methylated disaccharide and identification of the hydrolysis products. 200 ml of a 5% solution of hydrochloric acid was poured over 15 g of octamethylglucosido-2-galactose. The resulting mixture was kept at 80-85° for 1 hour and then boiled for 2 hours. The solution was neutralized with a dilute solution of sodium hydroxide and then evaporated to small volume. The reduced solution was treated five times with 50-ml batches of chloroform. The chloroform extracts were combined, desiccated, and evaporated, resulting in the crystallization of 2,3,4,6-tetramethylglucose with a m.p. of 93-95°; $\alpha_D^{20} + 84.5°$ (in chloroform, C = 1.2). The yield was 6.0 g. The 2,3,4,6-tetramethylglucose was identified via its anilide with a m.p. of 137-139°; $\alpha_D^{20} + 233.8°$ (in acetone, C = 2.1).

0.2007 g subs.: 8.4 ml $N_2$ (16°, 730 mm); 0.2010 g subs.: 8.1 ml $N_2$ (16°, 730 mm). Found %: N 4.81, 4.59. $C_{16}H_{25}O_5N$. Calc. %: N 4 50.

The solution left after the 2,3,4,6-tetramethylglucose had been extracted with chloroform was evaporated under reduced pressure to dryness. The residual syrup was dissolved in 300 ml of bromine water, the resultant solution being left to stand exposed to light for 3 days, with frequent stirring. Then the solution was thoroughly boiled to eliminate the bromine and neutralized with lead acetate, the excess lead being precipitated out of the filtered solution with hydrogen sulfide, and the solution being again neutralized with calcium carbonate. The

filtrate was evaporated to small volume, the flocs of the calcium salt of 3,4,6-trimethylgalactonic acid settling out when absolute ethyl alcohol was added.

The salt was decomposed with a calculated quantity of oxalic acid, and the filtered solution was evaporated to dryness. The residue was the lactone of 3,4,6-trimethylgalactonic acid. The rapid change of its angle of rotation identified it as the $\delta$-lactone; $\alpha \frac{20}{D} + 104.8 \rightarrow + 24.8°$ (in water, within 2 minutes).

0.1540 g subs.: 0.2781 g $CO_2$; 0.1035 g $H_2O$; 0.1121 g subs.: 0.3556 g AgI. Found %: C 49.19; H 7.51; $OCH_3$ 42.60. $C_9H_{16}O_6$. Calc. %: C 49.09; H 7.28; $OCH_3$ 42.27.

Methylating the lactone of 3.4.6-trimethylgalactonic acid yielded the $\delta$-lactone of 2,3,4,6-tetramethyl-d-galactonic acid, well known in the literature, with a m.p. of 160-161°; $\alpha \frac{20}{D} + 144.2° \rightarrow 25.1°$ (in water, within 2 minutes). The lactone was identified as its amide, with a m.p. of 119-120°; $\alpha \frac{20}{D} + 38.1°$ (in acetone).

0.1521 g subs.: 6.4. ml $N_2$ (16°, 730 mm); 0.1910 g subs.: 7.7 ml $N_2$ (16°, 730 mm). Found %: N 4.78, 4.61. $C_{10}H_{21}O_6N$. Calc. %: N 4.44.

## SUMMARY

1. A new disaccharide — glucosido-2-galactose — has been synthesized.

2. Condensing 2,3,4,6-tetraacetylglucose with 1,3,4,6-tetraacetylgalactose in the presence of zinc chloride and phosphoric anhydride yields the octaacetate of glucosido-2-galactose; saponification of the octaacetate yields the disaccharide.

## LITERATURE CITED

[1] A. M Gakhokidze, J. Gen. Chem. 11, 117 (1941).

[2] A. M. Gakhokidze, Trans. Tbilisi Pedagog. Inst. 1941, 1, 327.

[3] A. M. Gakhokidze, Proc. Georgian Acad. Sci. 9, 565 (1948).

[4] A. M. Gakhokidze, J. Gen. Chem. 16, 169 (1946).

[5] A. M. Gakhokidze, Proc. Georg. Acad. Sci. 10, 85 (1949).

[6] E. Fischer, K. Delbruck, Ber., 42, 2776 (1909).

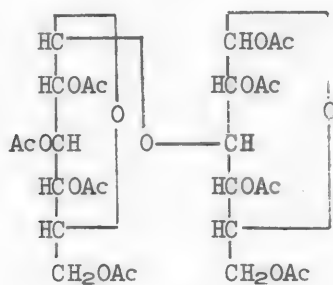[7] P. Brigl, Z. phys. Chem., 116, 1 (1921).

# ISOMERIZATION OF THE DISACCHARIDES

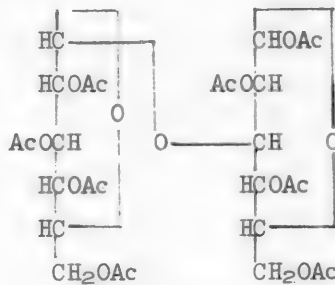## I.  IZOMERIZATION OF GLYCOSIDO-3-GLUCOSE

A. M. Gakhokidze and I. A. Gvelukashvili

The disaccharides have been synthesized by chemical as well as biochemical methods.  The reactions that lead to the conversion of one disaccharide into another may also come under the heading of disaccharide syntheses.  A first instance of a reaction of this type is the conversion of cellobiose into glucosido--4-mannose [1].  In his paper Hudson [2] showed that one disaccharide can be converted into another, stereoisomeric, disaccharide by the action of aluminium chloride, the hydroxyl groups and hydrogen atoms exchanging their positions at the 2 and 3 carbon atoms in the reducing part of the disaccharide.
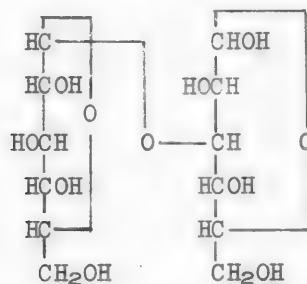
Our research had as its objective the use of askanite for the isomeric conversions of disaccharides.  In these tests we employed the disaccharide glucosido--3-glucose [3].  The glucosido-3-glucose was isomerized in organic solvents, so that the disaccharide was first acetylated.  The resulting octaacetate of the disaccharide (I) was dissolved in anhydrous chloroform, the solution being mixed with askanite and machine-agitated.  The chloroform was filtered and evaporated.  The crystals recovered were recrystallized a few times from ethyl alcohol to eliminate the original acetate.  As analysis indicated, these crystals were the octaacetate of glucosido-3-mannose (II).  Saponifying the octaacetate yielded glucosido-3--mannose (III).

$$
\begin{array}{cc}
\text{HC} & \text{CHOAc}\\
\text{HCOAc} & \text{HCOAc}\\
\text{AcOCH}\quad \text{O} & \text{CH}\quad \text{O}\\
\text{HCOAc} & \text{HCOAc}\\
\text{HC} & \text{HC}\\
\text{CH}_2\text{OAc} & \text{CH}_2\text{OAc}
\end{array}
$$

(I)

$$
\begin{array}{cc}
\text{HC} & \text{CHOAc}\\
\text{HCOAc} & \text{AcOCH}\\
\text{AcOCH}\quad \text{O} & \text{CH}\quad \text{O}\\
\text{HCOAc} & \text{HCOAc}\\
\text{HC} & \text{HC}\\
\text{CH}_2\text{OAc} & \text{CH}_2\text{OAc}
\end{array}
$$

(II)

$$
\begin{array}{cc}
\text{HC} & \text{CHOH}\\
\text{HCOH} & \text{HOCH}\\
\text{HOCH}\quad \text{O} & \text{CH}\quad \text{O}\\
\text{HCOH} & \text{HCOH}\\
\text{HC} & \text{HC}\\
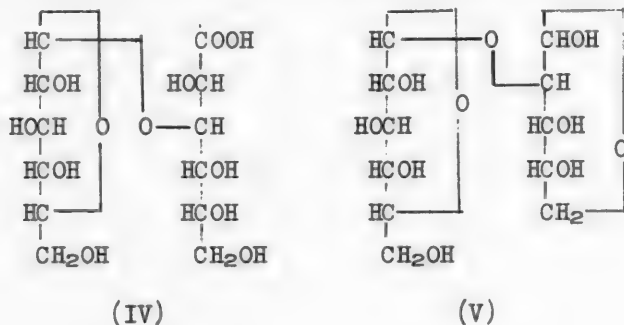\text{CH}_2\text{OH} & \text{CH}_2\text{OH}
\end{array}
$$

(III)

Oxidizing the disaccharide with bromine water yielded glucosido-3-mannonic acid (IV), hydrolysis of which yielded glucose, on the one hand, and mannonic acid, on the other. The mannonic acid was identified via its acetate.

```
   HC————   COOH          HC————O  CHOH
   HCOH  |   HOCH          HCOH  |  CH
   HOCH  O  O——CH       O  HOCH  O  HCOH
   HCOH  |   HCOH          HCOH  |  HCOH    O
   HC————   HCOH          HC————   CH2
   CH2OH    CH2OH          CH2OH
        (IV)                      (V)
```

Oxidizing the calcium salt of glucosido-3-mannonic acid with hydrogen peroxide in the presence of an iron salt yielded glucosido-2-d-arabinose (V). Glucosido-2-d-arabinose yields only a hydrazone, which is evidence of the location of the connecting oxygen bridge in this disaccharide (1,2) and in the synthesized glucosido-3 mannose (1,3).

Thus we see that the position of the connecting oxygen bridge in glucosido--3-glucose remains unchanged during isomerization.

<div align="center">EXPERIMENTAL</div>

1. Acetylating glucosido-3-glucose. A mixture of 20 g of glucosido-3-glucose (m.p. 162°), 10 g of dehydrated sodium acetate, and 150 g of freshly distilled acetic anhydride was refluxed, with frequent stirring, in a round-bottomed flask on a water bath for 3 hours. The hot liquid mass was added a drop at a time to 2 liters of ice water. The precipitated crystals were pulverized and kept under water until the next day to decompose the acetic acid. The filtered crystals were washed with cold water and recrystallized from ethyl alcohol. The yield was 31.4 g, or 78% of the theoretical.

M.p. 149-150°.

0.1319 g subs.: 15.5 ml 0.1 N NaOH; 0.2798 g subs.: 32.9 ml 0.1 N NaOH. Found %: $COCH_3$ 49.40, 49.53. $C_{28}H_{38}O_{19}$. Calc. %: $COCH_3$ 49.25.

2. Isomerizing glucosido-3-glucose acetate. 30 g of the octaacetate of glucosido-3-glucose was placed in 400 ml of anhydrous chloroform in a 1-liter round-bottomed flask fitted with a reflux condenser, and 100 g of dry askanite was added. The resulting mixture was agitated in the cold for 10 days. Toward the end the contents of the flask were heated to 70°. The askanite was filtered out of the faintly colored solution, which was evaporated to a thick syrup. The residual mass crystallized after a few hours. Microscopic examination of the crystals after they had been recrystallized from ethyl alcohol showed that they were not homogeneous, being apparently contaminated with the original product. The crystals were finally purified chromatographically on alumina.

M.p. 142-143°; $\alpha_D^{20}$ + 35.6° (in chloroform).

0.1522 g subs.:  17.6 ml 0.1 N  NaOH;  0.1997 g subs.:  23.2 ml 0.1 N
NaOH.  Found %:  $COCH_3$ 50.15, 49.99.  $C_{28}H_{38}O_{19}$.  Calc. %:  $COCH_3$ 49.25.

The free disaccharide was secured by saponifying the disaccharide acetate.

M.p. 165°;  $\alpha\frac{20}{D}$ + 27.9° (in water).

0.01 g subs.:  0.1 g camphor:  $\Delta t$ 11.3°;  0.01 g subs.:  0.1 g camphor:
$\Delta t$ 11.4°.  Found:  $\underline{M}$ 355, 350.  $C_{12}H_{22}O_{11}$.  Calc.:  $\underline{M}$ 342.

3.  Oxidation of the disaccharide and hydrolysis of the resulting acid.
18.5 g of the new disaccharide we had synthesized was dissolved in 300 ml of
bromine water, the resulting solution being exposed to light for 5 days with
frequent stirring.  Then the boiling solution was neutralized with calcium
carbonate.  The excess calcium carbonate was filtered out, and the solution
was evaporated to a minimum.  Gradually adding absolute ethyl alcohol to the
resulting solution threw down flocs of a calcium salt of the bionic acid.  The
precipitate was filtered out and recrystallized from hot water to refine it.
The yield was 16.3 g, or 81% of the theoretical.

0.2989 g subs.:  0.0210 g CaO;  0.3595 g subs.:  0.0294 g CaO.  Found %:
Ca 5.01, 5.87.  $(C_{12}H_{21}O_{11})_2$Ca.  Calc. %:  Ca 5.30.

Precipitating the calcium from 5 g of the calcium salt with a calculated
quantity of oxalic acid, followed by evaporating the filtered solution, yielded
the bionic acid as a syrup.  Then the bionic acid was boiled with a 5% solution
of sulfuric acid to decompose it.  The solution was neutralized, while boiling,
with calcium carbonate and then filtered.  Gradually adding absolute ethyl alco-
hol to the thickened solution threw down flocs of calcium mannonate.  The calcium
salt was purified by recrystallization from hot water.

After the calcium mannonate was filtered out, the solution was boiled with
5 ml of acetic acid and 5 g of pheylhydrazine.  Yellow crystals settled out of
the solution as it cooled.  The crystals were filtered out and purified by re-
crystallization from ethyl alcohol.  The  melting point of the pure substance
was 204 - 206°.  The mixed melting point with a known sample of the glucosazone
exhibited no depression.

4.  Oxidizing glucosido-3-mannonic acid.  5 g of the calcium salt of
glucosido-3-mannonic acid was dissolved in 100 ml of water.  Solutions of 1.5
g of ferric sulfate in 20 ml of water and 1.9 g of barium acetate in 20 ml of
water were added to the resulting solution after it had been heated to 70°.
The reaction mixture was vigorously stirred, and 30 ml of a 30% perhydrol solu-
tion was gradually added.  Three hours later another 10 ml of perhydrol was
added to the solution.  Then the precipitate was filtered out, and the solution
was evaporated at reduced pressure to the thickness of a syrup.  The syrup was
mixed with 300 ml of a 1:1 methanol-acetone mixture.  The insoluble matter was
filtered out of the solution, which was evaporated to syrupy thickness.  Yellow
crystals were thrown down when the residue was mixed with absolute methanol.
The next day the crystals were filtered out and dried.  The yield was 1.7 g, or
50% of the theoretical.

M.p. 149-150°;  $[\alpha]\frac{20}{D}$ + 29.5° (in water).

0.0895 g subs.:  0.1416 g $CO_2$;  0.0484 g $H_2O$;  0.1009 g subs.:  0.1542 g
$CO_2$;  0.0621 g $H_2O$.  Found %:  C 42.93, 42.20;  H 6.01, 6.90.  $C_{11}H_{20}O_{10}$.
Calc. %:  C 42.30;  H 6.41.

Acetylating glucosido-2-d-arabinose.

M.p. 138-140°;  $[\alpha]_D^{20}$ + 46.6° (in chloroform).

0.1045 g subs.:  12.4 ml 0.1 N. NaOH;  0.1510 g subs.:  17.6 ml 0.1 N solution of NaOH.  Found %:  $COCH_3$ 49.85, 50.21.  $C_{25}H_{34}O_{17}$.  Calc. %: $COCH_3$ 49.60.

When glucosido-2-d-arabinose was boiled with phenylhydrazine in the presence of acetic acid, followed by evaporation of the solution to small volume, the crystals of glucosido-2-d-arabinose hydrazone settled out;  they were refined by recrystallization from alcohol.  M.p. 177-181°.

0.1259 g subs.:  7.9 ml $N_2$ (15°, 738 mm);  0.1518 g subs.:  9.8 ml $N_2$ (15°, 738 mm).  Found %:  N:  7.25, 7.49.  $C_{17}H_{26}O_9N_2$.  Calc. % N 6.96.

The glucosido-3-mannonic acid was boiled with dilute sulfuric acid, glucose and mannonic acid were produced.  The resulting solution was neutralized with calcium carbonate and filtered.  A few milliliters of absolute ethyl alcohol were added to the thickened filtrate, causing flocs of calcium mannonate to settle out.

0.1579 g subs.:  0.0211 g CaO;  0.2489 g subs.:  0.0315 g CaO.  Found %: Ca 9.57, 9.05.  $(C_6H_{11}O_7)_2Ca$.  Calc. %:  Ca 9.30.

Decomposing the calcium mannonate with a calculated quantity of oxalic acid, followed by evaporating the filtered solution, yielded crystals of the lactone of mannonic acid, with a m.p. of 149-150°;  $[\alpha]_D^{20}$ + 50.8° (in water), which agrees with the figures in the literature [4].  The mixed melting point with a known sample of the lactone of mannonic acid exhibits no depression.

0.1500 g subs.:  0.2525 g $CO_2$.  0.0747 g $H_2O$;  0.2110 g subs.:  0.3597 g $CO_2$;  0.0939 g $H_2O$.  Found %:  C 46.09, 46.61;  H 5.51, 5.01.  $C_6H_{10}O_6$. Calc. %:  C 46.05;  H 5.68.

Phenylhydrazide:  m.p. 213-214°;  $[\alpha]_D^{20}$ + 15.8° (in water).

0.2201 g subs.:  20.3 ml $N_2$ (16°, 740 mm);  0.3510 g subs.:  32.4 ml $N_2$ (16°, 740 mm).  Found %:  N 9.98, 10.09 $C_{12}H_{18}O_6N_2$.  Calc. %:  N 9.75.

The tetraacetate of mannonolactone had a m.p. of 119-120°;  $[\alpha]_D^{20}$ + 51.4° (in chloroform).  The mixed melting point with a known sample of the tetraacetate of mannonolactone exhibited no depression.

0.1020 g subs.:  11.5 ml 0.1 N  NaOH:  0.1100 g subs.:  12.6 ml 0.1 N. NaOH.  Found %:  $COCH_3$ 49.01, 49.33.  $C_{14}H_{18}O_{10}$.  Calc. %:  $COCH_3$ 49.65.

## SUMMARY

1.  Glucosido-3-mannose has been produced by agitating a chloroform solution of acetylated glucosido-3-glucose with askanite.

Glucose-3-mannose has been synthesized from acetylated glucosido-3-mannose.

2.  Oxidation of the calcium salt of glucosido-3-mannonic acid with hydrogen peroxide yields glucosido-2-d-arabinose.

3.  The glucosido-3-mannose and glucosido-2-d-arabinose have been identified via several of their derivatives.

## LITERATURE CITED

[1]  M. Bergmann, R. Schotte, Ber., 54, 1564 (1921);  S. N. Danilov and P. T.

Pastukhov, <u>J. Gen. Chem. 16</u>, 923 (1946).

[2]  C. H. Hudson, <u>J. Am. Chem. Soc., 58</u>, 2534 (1936).

[3]  A. M. Gakhokidze, <u>J. Gen. Chem. 16</u>, 169 (1946).

[4]  E. Fischer, L. Hirschberger, <u>Ber., 22</u>, 3220 (1889);  O. Hedenburg, <u>J. Am. Chem. Soc., 37</u>, 345 (1915).


March 7, 1950.                    The A. S. Pushkin Pedagogical Institute
                                  of Tbilisi.

# SYNTHESIS AND PROPERTIES OF 1,1-DIPHENYLPROPENE-1 OXIDE

V. I. Pansevich-Kolyada and L. I. Timoshek

It is common knowledge that one of the principal methods of preparing alpha oxides is the reaction of alkalies with the halohydrins of alpha glycols. The conditions required for carrying out this reaction and the latter's velocity vary with the nature and concentration of the bases employed, and particularly with the structure of the original halohydrins. The aliphatic alpha oxides are produced by processing the respective halohydrins with aqueous, and even better, with alcoholic solutions of alkalies, comparatively little heat being required [1]. It is even easier to produce alpha oxides with aromatic radicals, some of them being produced when ether solutions of the respective halohydrins are merely agitated with powdered potassium hydroxide [2].

Eltekov [3] showed that the aliphatic alpha oxides which have a tertiary carbon atom in the oxide ring are hydrated very energetically, a large quantity of heat being evolved in some instances (isobutylene and tetramethylethylene oxides). N. A. Prilezhaev [4] secured the oxide of 2-methylhepten-2-one-6, which added water so quickly as to hinder its isolation. When the oxide ring contains primary or secondary carbon atoms, the oxides are hydrated very much more slowly, some of them requiring prolonged heating to 100° under pressure. The weight of the oxide molecules likewise affects their reaction with water [3]. Provided the structures of the oxides are identical, the alpha oxides of higher molecular weight will be hydrated more quickly. It has also been found [5] that the reaction of alpha oxides with water is strongly catalyzed by the hydrogen ions of acids, thus hydrating many oxides at ordinary temperature.

Another interesting feature of alpha oxides that is of practical importance is their ability to undergo isomeric transformations into aldehydes or ketones, depending upon the location of the oxide ring [6]. This latter process requires differing conditions that vary with the structure of the alpha oxides, and, conversely, under different conditions the alpha oxides may be isomerized into aldehydes or ketones or mixtures of the two [7]. The alpha oxides are isomerized exceptionally readily when certain substances are present, which catalyze this reaction, particularly acids [8]. The phenyl radical greatly increases the tendency of the oxides to undergo hydration and isomeric transformations. Phenylethene, 3-phenylpropene-1, 2-phenylpropene-1, and other alpha oxides, for example, are isomerized to the respective aldehydes or ketones by the action of hydrogen ions, as well as when they are distilled at atmospheric pressure, while 1,1-di--phenylethene is converted into the isomeric diphenylacetaldehyde even when distilled in vacuo [9].

The reports on 1,1-diphenylpropene-1 oxide are contradictory, however. Stoermer [10] heated 1,1-diphenyl-2-phenoxypropanol-1 — $(C_6H_5)_2COH-CH(OC_6H_5)CH_3$ with alcoholic potassium hydroxide to 220° under pressure and secured a mixture of products, one of which was a crystalline substance with a m.p. of 67° and a b.p. of 300° (with slight decomposition). The author believed that this compound was 1,1-diphenylpropene-1 oxide, which is not convertible into the isomeric

ketone, but Stoermer's findings are obviously wrong. Levy and Lagrave [11] also secured 1,1-diphenylpropene-1 oxide by oxidizing that hydrocarbon with benzoyl peroxide. According to them, this oxide is a crystalline substance, melting at 34° and isomerizing to 1,1-diphenylpropanone-2 when distilled slowly at atmospheric pressure.

One of the present authors [12] brominated 1,1-diphenylpropanol-1 in 80% acetic acid and secured a high yield of 1,1-diphenyl-2-bromopropanol-1. This bromohydrin was unknown in the literature, and we were interested in learning how it behaved with an alkali and in continuing a study of the properties of the 1,1-diphenylpropene-1 oxide that we expected to prepare:

$$(C_6H_5)_2C(OH)CHBrCH_3 \rightarrow (C_6H_5)_2C\text{———}CHCH_3 + HBr.$$
$$O$$
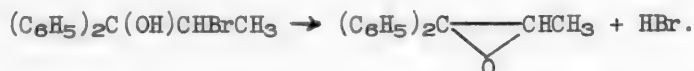
The action of an alcoholic solution of KOH upon the bromohydrin in ethyl alcohol yielded an oily product, which yielded two substances when distilled. The first one boiled at 131-132° (2 mm), its analysis being the equivalent of $C_{15}H_{14}O$. When we added this substance to a 0.1 N solution of sulfuric acid, we secured a crystalline compound with a m.p. of 90-90.5°. Its analysis was equivalent to $C_{15}H_{16}O_2$, which is doubtless the formula of 1,1-diphenylpropane-diol-1,2 in this instance. In our experiment the only way for that glycol to be formed is by hydration of the saponification product of the bromohydrin — 1,1-diphenylpropene-1 oxide:

$$(C_6H_5)_2C\text{———}CHCH_3 \rightarrow (C_6H_5)_2COHCHOHCH_3.$$
$$O$$
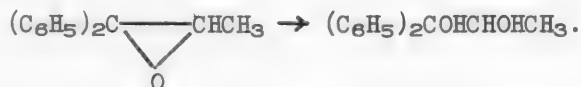
It should be noted that this oxide is also hydrated slowly in pure water, but is not hydrated in an alkaline medium.

The second substance, which distilled at 146-146.5° (2 mm), soon crystallized, with a m.p. of 43-44°. It exhibited no active hydrogen and reacted with semicarbazide. The analysis of this substance was the equivalent of $C_{15}H_{14}O$, which could only be the formula of the ketone formed by the isomerization of 1,1-diphenylpropene-1 oxide:

$$(C_6H_5)_2C\text{———}CHCH_3 \rightarrow (C_6H_5)_2CHCOCH_3.$$
$$O$$
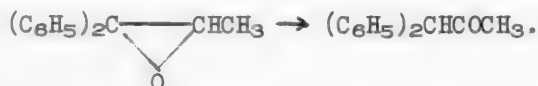
The structure of the synthesized compound was finally established by oxidizing it with nitric acid and a 1% permanganate solution. The oxidation products were found to contain benzophenone and diphenylacetic, acetic, and formic acids, which is proof of the formula 1,1-diphenylpropanone-2.

It should be noted that the literature states [13] that 1,1-diphenylpropanone-2 exists in two modifications: a low-melting one (m.p. 44-46°) and a high-melting one (m.p. 61°). The former is sometimes produced in recrystallization from alcohol, changing into the second one upon long storage; the high-melting one is produced most often and is not converted into the first form. In our test all of the 1,1-diphenylpropanone-2 was secured with a m.p. of 43-44°, its melting point remaining the same after recrystallization from ethyl alcohol and after nine months of storage. Hence, heating the oxide to 135° (2 mm) isomerized it to the corresponding ketone —

1,1-diphenylpropanone-2, while it is hydrated in an aqueous medium, especially when hydrogen ions are present, yielding the glycol 1,1-diphenylpropanediol-1,2. Inasmuch as the yield of 1,1-diphenylpropene-1 oxide and of 1,1-diphenylpropanone-2 (or, if desired, of 1,1-diphenylpropanediol-1,2) is nearly quantitative, the method we have outlined may be used to advantage in producing these substances for organic synthesis.

## EXPERIMENTAL

Action of an alcoholic alkali on 1,1-diphenyl-2-bromopropanol-1. The bromohydrin $(C_6H_5)_2C(OH)CHBrCH_3$ was secured by brominating the tertiary alcohol 1,1--diphenylpropanol-1 in 80% acetic acid; its m.p. was 57°.

59.5 g of the bromohydrin was dissolved in ethyl alcohol, and about 60 g of 20% alcoholic KOH was slowly added. The alcoholic solution was diluted with water, the oil that settled out being separated, and the residue extracted with ether. The oil was combined with the ether extract, and the ether was driven off after desiccation over calcined potash. The remaining faintly yellowish oily liquid, totalling 42 g, was distilled twice at 2 mm, the following fractions being collected: 1) 130-131°, 1.0 g; 2) 131-132°, 9.0 g; 3) 132-136°, 1.5 g; 4) 146-146.5°, 28.5 g; plus a residue of 2.0 g in the distilling flask.

Fraction 2, b.p. 131-132° (2 mm), was a colorless liquid with a faint odor, which was oxidized very slowly by a 1% permanganate solution, reacted with bromine (evolving HBr), did not evolve methane when reacted with methylmagnesium iodide, and did not react with semicarbazide.

$n_D^{20}$ 1.5740; $d_4^{20}$ 1.0739; $MR_D$ 66.01. $C_{15}H_{14}OF_6$. Calc. 63.71.

0.1894 g subs.: 0.5965 g $CO_2$; 0.1172 g $H_2O$; 0.1756 g, 0.3672 g subs.: 23.83 g benzene: $\Delta$t 0.20, 0.41°. Found %: C 85.89; H 6.92. M 189.37, 193.17. $C_{15}H_{14}O$. Calc. %: C 85.71; H 6.66. M 210.

Hydration of 1,1-diphenylpropene-1 oxide. 3 g of the oxide was added to 15 ml of 0.1 N sulfuric acid. Hydration commenced after 30 to 40 minutes of agitation, the entire flask being full of snow white crystals aggregated into stars after 24 hours had elapsed.

The crystals were readily soluble in ether, methanol, ethyl alcohol, benzene, and acetic acid, dissolving more sparingly in petroleum ether, from which they were recrystallized. Their m.p. was 90-90.5° after they had been dried in a desiccator over sulfuric acid.

0.0798 g, 0.0883 g subs.: 15.71 ml, 17.64 ml $CH_4$ (0°, 760 mm); 0.1116 g, 0.2963 g subs.: 20.99 g benzene: $\Delta$t 0.129, 0.311°. Found %: OH 15.04, 15.27. M 211.9, 233.3. $C_{15}H_{16}O_2$. Calc. %: OH 14.91. M 228.

Fraction 4, b.p. 146-146.5° (2 mm), crystallized within 3 hours, its m.p. being 43-44°; the melting point did not change after recrystallization from ethyl alcohol. It was freely soluble in methanol, benzene, and chloroform. It decolorized a 1% solution of $KMnO_4$ slowly and decolorized bromine faster than did the oxide, though with the liberation of HBr, as in the case of the oxide. It did not liberate methane when reacted with methylmagnesium iodide, but reacted with semicarbazide to form a semicarbazone, the m.p. of which was 163-163.5° after recrystallization from methanol.

$n_D^{20}$ 1.5793; $d_4^{20}$ 1.0813; $MR_D$ 64.56. $C_{15}H_{14}O_6$. Calc. 64.28.

0.1737 g, 0.2019 g subs.: 0.5560 g, 0.6325 g $CO_2$; 0.1078 g, 0.1225 g

$H_2O$;  0.1157 g, 0.3568 g subs.:  22.29 g benzene: $\Delta t$ 0.135, 0.395°.
Found %:  C 85.52, 85.63;  H 6.8    6.79.  M 198.1, 208.7.  $C_{15}H_{14}O$.
Calc. %:  C 85.71;  H 6.66.  M 210.

Oxidizing 1,1-diphenylpropanone-2 with nitric acid. 24 ml of nitric acid
(sp. gr. 1.3) and 15 ml of water were added to 4 g of the substance.  The mix-
ture was boiled for 5 hours and then carefully neutralized with potash, the
volatile neutral products of oxidation being driven off with steam.  The ether
extract yielded benzophenone, the semicarbazone of which had a m.p. of 163.5-
165°.  The mixed melting point with the known product exhibited no depression.
The salts of the acids were decomposed with weak sulfuric acid, and the vola-
tile acids were driven off.  The solution of these acids was concentrated and
processed with silver carbonate.  Heating threw down an abundant black precipi-
tate, evidence of the presence of formic acid.  Crystallization of the silver
salts yielded three fractions, analysis of which gave the following results:

Fraction I 0.045 g subs.: 0.0225 g Ag;  Fraction II 0.0971 g subs.:
0.0607 g Ag;  Fraction III 0.0498 g subs.:  0.0321 g Ag.  Found %:  Ag
50.0, 62.51, 64.45.  $CH_3COOAg$.  Calc. %:  Ag 64.64.

The residue left after the volatile acids had been distilled was extracted
with ether.  Driving off the ether left behind a thick, dark-red, resinous mass,
out of which crystals of a non-volatile acid, slightly soluble in benzene, settled
out 24 hours later.  The resinous portion was slowly eluted in the cold with
small portions of benzene, the acid then being recrystallized from the latter.
The acid had a m.p. of 145-146° with partial sublimation, which agrees with the
figures [14] given for diphenylacetic acid.  Thus, oxidation yielded benzophenone
and formic, acetic, and diphenylacetic acids.

Oxidizing 1,1-diphenylpropanone-2 with a 1% solution of permanganate.  600
ml of a 1% solution of permanganate was added to 4 g of the substance portionwise
as it was decolorized (which occurred with great difficulty).  The presence of
benzophenone among the neutral reaction products was demonstrated by the follow-
ing findings:  m.p. 47.5-48°;  no depression of the mixed melting point with a
known sample of benzophenone;  and semicarbazone m.p. 164 165°.

The salts of the acids were decomposed with sulfuric acid, and the volatile
acids were distilled.  Processing the solution of the volatile acids with silver
carbonate yielded a minute black precipitate plus two fractions of silver salts.

Fraction I 0.1113 g subs.:  0.0679 g Ag;  Fraction II 0.1207 g subs.:
0.0779 g Ag.  Found %:  Ag 61.06, 64.54.  $CH_3COOAg$.  Calc. %:  Ag 64.64.

The non-volatile acids were extracted with ether;  driving off the ether
yielded a minute quantity of a crystalline acid that sublimed and had a m.p. of
144-145.5° after recrystallization from benzene.

Thus, oxidation of 1,1-diphenylpropanone-2 with a 1% permanganate solution
yielded benzophenone and formic, acetic, and phenylacetic acids.  The process
takes place chiefly at the bond between the carbonyl group and the first carbon
atom.

### SUMMARY

1.  It has been found that 1,1-diphenylpropene-1 oxide is produced with
great ease, in a nearly theoretical yield, by 1,1-diphenyl-2-bromopropanol-1
with an alcoholic alkali.

2.  1,1-Diphenylpropene-1 oxide is isomerized to 1,1-diphenylpropanone-2 when distilled in vacuum at 135° (2 mm), and is hydrated very rapidly to 1,1-diphenylpropanediol-1,2  in an acid medium.

## LITERATURE CITED

[1]  A. P. Eltekov, J. Russ. Chem. Soc. 5, 10, 81, 82, 211 (1873); 14, 355 (1882); Wurtz, Comptes rend. 45, 228 (1857); Ann., 104, 174 (1857); Ann. Chim. Phys., 55, 400 (1859); Ann., 110, 125, (1859); M. Kashirsky, J. Russ. Chem. Soc., 14, 355 (1882).

[2]  Tiffeneau, Comptes rend., 140, 1459, 1595, 1597 (1905); 146, 697 (1908); Klages, Ber., 38, 1970 (1905); 39, 1754 (1906).

[3]  A. P. Eltekov, J. Russ. Chem. Soc. 14, 355 (1882).

[4]  N. A. Prilezhaev, J. Russ. Chem. Soc. 43, 609 (1911).

[5]  N. A. Prilezhaev,  Organic peroxides and their use in oxidizing unsaturated compounds, p. 159. (1912); Zimakov. Ethylene oxide, p. 62 (1947). Henry, Comptes rend., 144, 1404 (1907).

[6]  M. Kashirsky. J. Russ. Chem. Soc. 13, 76 (1881); K. A. Krasusky. Research on isomeric transformations in which organic oxides take part. (1902); N. A. Prilezhaev. Op. Cit. p. 151, (1912).

[7]  S. N. Danilov, J. Russ. Chem. Soc. 51, 97 (1919); 59, 187 (1927).

[8]  K. A. Krasusky, J. Russ. Chem. Soc. 34, 537 (1902); N. A. Prilezhaev, Op. cit., 155. (1912).

[9]  Klages, Ber., 39, 1755 (1906).

[10] Stoermer, chem. zentr., 1906, II, 524.

[11] Levy and Lagrave, chem. zentr. 1925, I, 1427.

[12] V. I. Pansevich-Kolyada and N. A. Prilhezhaev, Bull. All-Union Mendeleev Chem. Soc. 1939, No. 10, 35; J. Gen. Chem., 21, 517 (1951).

[13] Beilstein, VII, 448.

[14] Beilstein, IX, 673.

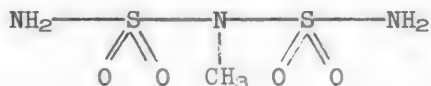# THE HYDROLYSIS OF 2-METHYLIMIDOSULFONAMIDE AND MONOMETHYLSULFONAMIDE

A. V. Kirsanov and Yu. M. Zolotov

The hydrolysis of 2-methylimidosulfonamide is much easier than that of the free imidosulfonamide [1]. Hydrolysis is nearly complete within 30 minutes in an approximately 0.25 N aqueous solution at 30°. When a weighed sample of 2-methylimidosulfonamide is dissolved in water at 15°, the solution being chilled to +5° within a minute and then evaporated in vacuum to dryness within 15 minutes at temperatures ranging from 0 to +5°, about 60% of the 2-methylimidosulfonamide is hydrolyzed. Hence, the experimental method of determining the velocity constant of hydrolysis, which was successfully employed for the free imidosulfonamide [1], is unsuited to a quantitative determination of the velocity constant of hydrolysis of 2-methylimidosulfonamide, though it is absolutely certain that 2-methylimidosulfonamide is hydrolyzed incomparably faster than the free imidosulfonamide is.

It has been previously established that the sodium salt of imidosulfonamide is hydrolyzed very slowly in boiling aqueous solutions [1]. We thus get the following series: sodium salt of imidosulfonamide (hydrolyzed rather slowly) — free imidosulfonamide (hydrolyzed rather quickly) — 2-methylimidosulfonamide (hydrolyzed extremely quickly). These findings are the basis for the conclusive deduction that the imidosulfonamide ion is stable in aqueous solutions, whereas the imidosulfonamide molecule is readily hydrolyzed in aqueous solutions. In the case of the sodium salt, the solution contains principally ions, and hydrolysis is slow. A solution of the free imidosulfonamide contains both ions and molecules, so that hydrolysis is faster. In the case of 2-methylimidosulfonamide, however, the solution contains nothing but molecules, so that hydrolysis is extremely rapid. It follows that the structure of the ion differs from that of the molecule. The stability of the imidosulfonamide ion is due to the fact that it possesses the following structure:

$$H_2N - S - N - S - NH_2$$

in contrast to 2-methylimidosulfonamide, the structure of which is:

$$NH_2 - S - N - S - NH_2$$
$$O \quad O \quad CH_3 \quad O \quad O$$

In other words, the N — S distance (between the central nitrogen atom and the sulfur atom) is shortest in the sodium salt of imidosulfonamide, and greatest in 2--methylimidosulfonamide. It would be extremely interesting to check these conclusions by X-rays or electronographically.

Large numbers of the tetraalkyl sulfonamides, trialkyl sulfonamides, and asymmetrical dialkyl sulfonamides have been synthesized by now and thoroughly studied [2]. Not a single monoalkyl sulfonamide has been known, however. This is why the hydrolysis of 2-methylimidosulfonamide is highly interesting, since it ought to yield,

as we have shown in one of our previous papers, monomethylsulfonamide, as follows:

$$NH_2-SO_2-N(CH_3)-SO_2-NH_2 \xrightarrow{+H_2O} NH_2SO_2OH + NH_2SO_2NHCH_3 .$$
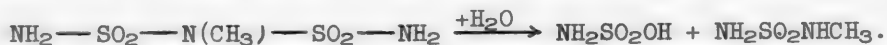
As a matter of fact, we succeeded in securing a practically quantitative yield of monomethylsulfonamide from the hydrolysis products of 2-methylimidosulfonamide, its properties being described in the experimental section.

## EXPERIMENTAL

Determination of the rate of hydrolysis of 2-methylimidosulfonamide. This was done as for the free imidosulfonamide [1]. I. A 0.4525 g sample was dissolved in 10 ml of water, heated for 30 minutes to $30 \pm 0.05°$, and so forth. Titration of the sulfamic acid required 2.29 ml of a 1N solution of sodium hydroxide. This indicated that 95.4% was hydrolyzed, i.e., nearly complete hydrolysis, in view of the fact that the accuracy of the method did not exceed 2-3%

II. A 0.4490 g sample was dissolved in 10 ml of water at 15°, the solution being chilled to +5° within a minute and then evaporated to dryness in vacuo at a temperature ranging from 0 to +5° for 15 minutes, and so forth. Titration required 1.43 ml of a 1N solution of sodium hydroxide. Thus 61.1% was hydrolyzed.

## Synthesis of Monomethylimidosulfonamide

0.01 mol (1.89 g) of 2-methylimidosulfonamide was dissolved in 10 ml of water, and the solution was quickly brought to a boil, after which it was immediately cooled to room temperature and quickly evaporated in vacuo at 30° to dryness. The crystalline residue was extracted three times with 20 ml portions of absolute ethyl acetate. The residue left after the solvent had been driven off in vacuum consisted of 1.05 g of large colorless prisms with a m.p. of 63-65°. The yield was therefore 95% of the theoretical. After recrystallization from a large quantity (see below) of boiling benzene, thin snow-white, silky needles up to 30 mm long, m.p. 65.5-66.0° (uncorr.).

Monomethylimidosulfonamide is readily soluble in water, alcohol, acetone, and ethyl acetate. The aqueous solutions are neutral.

Its solubility in diethyl ether at 20° is 90%. Its solubility in boiling benzene is 0.265%, and 0.043% at 25°.

23.71 mg substance: 9.43 mg $CO_2$; 11.59 mg $H_2O$; 26.22 mg substance: 10.46 mg $CO_2$; 12.86 mg $H_2O$; 5.95 mg substance: 1.314 ml $N_2$ (21°, 755 mm); 6.10 mg substance: 1.350 ml $N_2$ (21°, 755 mm); 0.1216 g substance: 0.2589 g $BaSO_4$; 0.1322 g substance: 0.2809 g $BaSO_4$.

Found: % C 10.85, 10.87; H 5.47, 5.49; N 25.48, 25.53; S 29.23, 29.17. $CH_6O_2N_2S$. Calc. %: C 10.90; H 5.49; N 25.45; S 29.12.

## SUMMARY

1. It has been shown that 2-methylimidosulfonamide is hydrolyzed much faster than the free imidosulfonamide.

2. The hypothesis is advanced that the high rate of hydrolysis of 2-methylimidosulfonamide is due to the great distance between the central nitrogen atom and the adjacent sulfur atoms and that the stability of the sulfonamide ion in aqueous solutions is due to the lessening of this distance.

3. Monomethylimidosulfonamide has been synthesized and described.

## LITERATURE CITED

[1]  A. V. Kirsanov and Yu. M. Zolotov, J. Gen. Chem. 19, 2201[*] (1949).

[2]  K. Wheeler,  E. Degering, J. Am. Chem. Soc., 66, 1242 (1944);  A. Fuhrman,  E. Degering, J. Am. Chem. Soc. 67, 1245 (1945); cf L. Audrieth and collab., Chem. Rev., 26, 49. for other literature on this problem.

Chair of Organic Chemistry,
The J. V. Stalin Metallurgical Institute of Dnepropetrovsk.

# SULFONATION AND SULFO ACIDS OF ACIDOPHOBIC COMPOUNDS

## XVIII. THE SULFONATION OF THIOPHENE

A. P. Terentyev and G. M. Kadatsky

In previous papers by one of the present authors [1] and in collaboration with L. A. Kasitsina [2] we have reported the results of our initial experiments on sulfonating thiophene and the alpha halogen thiophenes [3] with pyridine sulfotrioxide. They demonstrated that thiophene could be easily disulfonated under conditions in which its more acidophobic analogs — pyrrole and furan — yielded monosulfonic acids [1,2,4].

We have found that when thiophene is heated to 95-100° with pyridine sulfotrioxide, up to 28% of disulfo products are formed and up to 52% of the monosulfonic acid. Disulfonation is nearly complete (90% yield) at 130° (8 hours of catalysis). Using "acid" pyridine sulfotrioxide (adding 0.5% of sulfuric anhydride to the neutral reagent) speeds up this reaction and enables its temperature to be reduced to 95-100° (4-5 hours of catalysis).

The behavior of thiophene at high temperature very much resembles that of α-methylfuran, which also yields a disulfonic acid. The only way to effect monosulfonation of the latter compound was to react it for a long time with pyridine sulfotrioxide at 20-30° [2]. At this temperature the sulfonation of thiophene likewise involves the introduction of only one sulfo group:

$$\text{(thiophene)} + C_5H_5N \cdot SO_3 \longrightarrow \text{(thiophene)} - SO_3H \cdot NC_5H_5$$

though we could not secure a higher yield than 50%.

Thus, the decisive factor affecting the course of the reaction is the temperature, so that some way of modifying the reaction, without raising the temperature, had to be found to secure a better yield of thiophenesulfonic acid. Employing the acid pyridine sulfotrioxide yielded nothing new. Only by resorting to a new sulfonating agent — pyridine bissulfotrioxide — did we secure the desired result.

Pyridine bissulfotrioxide was prepared by reacting together equimolecular quantities of pyridine sulfotrioside and sulfuric anhydride. The latter was added either directly or dissolved in dichloroethane. The reaction was highly

189

exothermic. When the sulfotrioxide was used straight, the reagent was secured as a thick colorless liquid that solidified into a white crystalline mass with a m.p. of 83-85°. It fumed slightly when exposed to the air, reacted exothermally (but very quietly) with water, and underwent no change when heated to 150-160° for 24 hours. When the dichloroethane solution was used, a heavy liquid layer of the product separated out, which was converted into a low-fusible crystalline mass with difficulty. Each of these methods possesses its advantages. The first one yields the individual pyridine bissulfotrioxide, which dissolves in the substance to the sulfonated, the reaction taking place in a single phase. The second enables the sulfuric anhydride to be stored conveniently and its dosage to be measured accurately, but it involves retardation of the sulfonation reaction owing to the layering of the components.

Pyridine bissulfotrioxide reacted strongly with thiophene, yielding thiophenesulfonic acid. Sulfonation is 60% complete after 2 hours and 86% complete after 10. It is worthy of note that one molecule of this reagent reacts with two molecules of the substance to be sulfonated:

$$2 \left[\begin{array}{c} \\ S \end{array}\right] + C_5H_5N \cdot S_2O_6 \longrightarrow \left(\left[\begin{array}{c} \\ S \end{array}\right] - SO_3H\right)_2 \cdot C_5H_5N$$

i.e., all the sulfuric anhydride is used in the reaction. When pyridine sulfo-trioxide is used, 2 mols of it are required per mol of the substance, i.e. only half of the sulfuric anhydride goes to constitute the C — S bond, the rest remaining inactive, as it were.

The processing of the sulfo mass when the new reagent is employed is the same as that used with the pyridine sulfotrioxide. We have greatly simplified the procedure for preparing sulfochlorides. In the past, treating the reaction mass with barium carbonate yielded a barium salt, which was converted into a potassium salt, the latter being finally converted into the sulfochloride by the action of phosphorus pentachloride. We found that we could eliminate this sequence of reactions, treating the initial product with phosphorus pentachloride directly at 70-80° for 2 hours. The sulfochlorides are recovered from the reaction mass in the usual manner, the yields being satisfactory and the purity of the product adequate.

Thus, the use of pyridine sulfotrioxide and pyridine bissulfotrioxide to sulfonate thiophene has several advantages and produced better yields than the methods hitherto employed.

V Meyer [5] and L. Weitz [6] used concentrated sulfuric acid, for example, diluting it more than 100 times with ligroin to prevent the complete tarring of the thiophene. The black sulfo mass had to be processed at once, as it too tarred completely when allowed to stand. The yield of the thiophene sulfonate was about 45%. Use of fuming sulfuric acid [7] yielded similar results.

V. Steinkopf and T. Hopner [8] used chilled chlorosulfonic acid and obtained a 65% yield of the sulfochloride. But their procedure was also unsatisfactory, since no more than 15% (of the theoretical quantity) of the sulfochloride was recovered when the reaction mass was decomposed with ice. The rest of the sulfo-chloride was secured by neutralizing the aqueous layer with soda and processing the desiccated mixture of sodium thiophenesulfonate, sodium sulfate, and sodium chloride with phosphorus pentachloride.

V. Meyer [9] and H. Jackel [10] secured salts of thiophenesulfonic-2,4 acid by sulfonating barium thiophenesulfonate with oleum, followed by processing of the sulfo mixture. V. Steinkopf and T. Hopner [8] sulfonated the sulfochloride rather than the salt with 7% oleum, securing a low yield of a mixture of 2,4- and 2,5-disulfo products.

Thus, the use of "acid" pyridine sulfotrioxide at high temperature effects a single-stage synthesis of thiophenylsulfo derivatives, replacing the previous two-stage syntheses. The yield obtained is high, producing a mixture of the 2,4 and 2,5 isomers, with the former predominating. At a low temperature all the sulfonating agents we have employed yield alpha sulfo products.

<center>EXPERIMENTAL</center>

<center>Thiophenylsulfonic-2 Acid</center>

Sulfonation with pyridine sulfotrioxide. Synthetic thiophene was used in sulfonation. B.p. 83.7-84° at 748 mm; $d_4^{20}$ 1.0607; $n_D^{20}$ 1.5238.

2.75 g of thiophene and 5.1 g of pyridine sulfotrioxide were sealed into an ampoule. After the latter had lain for a month at 20-30°, a white crystalline mass formed. The usual processing with barium carbonate and steam distillation of the pyridine was followed by evaporation of the filtrate, the barium salt being dried at 130°. The yield was 3.8 g (50%, based on the thiophene used).

Sulfonation with pyridine bissulfotrioxide. A solution of 1.6 g of sulfuric anhydride in 16 ml of dichloroethane was gradually added, with stirring, to 3.2 g of pyridine sulfotrioxide. The mixture grew warm. The application of gentle heating is required to complete the reaction, a colorless layer of pyridine bissulfotrioxide being formed beneath the dichloroethane. Then the mixture was stirred as 3.1 g of thiophene was added, causing the mixture to grow warm. Ten hours later the mixture was treated with water at room temperature, and the dichloroethane layer was removed. The aqueous layer was treated with an excess of barium carbonate and evaporated to eliminate the pyridine. Filtration and evaporation yielded 7.37 g of the barium salt (86% of the theoretical yield, based on the thiophene used). Mercuration of the dichloroethane layer resulted in the nearly complete recovery of the unreacted thiophene.

Barium thiophenesulfonate is a finely crystalline white powder that is freely soluble in water. Reacting the salt with bromine water throws down an abundant precipitate of $BaSO_4$.

5.520 mg substance: 2.797 mg $BaSO_4$; 4.690 mg substance: 2.380 mg $BaSO_4$. Found %: Ba 29.82, 29.87. $C_8H_6O_6S_4Ba$. Calc. %: Ba 29.62.

The S- ($\alpha$- naphythyl) - thiuronate was prepared by mixing together saturated aqueous solutions of naphthylthiurone chloride and the barium sulfonate. The precipitate was recrystallized from water. M.p. 174.5-175°.

5.505 mg substance: 0.3822 ml $N_2$ (29°, 741 mm). Found %: N 7.65. $C_{11}H_{16}O_3N_2S_3$. Calc. % N 7.19.

2-Thiophene sulfochloride. 1) This was prepared from the potassium salt by heating it to 100° for 2 hours with an excess of phosphorus pentachloride and then pouring the reaction mass over ice. The crystals that formed were filtered out. M.p. 28-31°, but 31-32° after recrystallization from petroleum ether (b.p. 20-40°). Steinkopf gives the m.p. as 31.5-33° [8], while Weitz gives 28° [6]. 6.4 g of pyridine sulfotrioxide was placed in a 50-ml round bottomed flask, and 3.2 g of sulfuric anhdryide was added. The mixture heated up spontaneously to 90°, being converted into a thick, colorless liquid, which

solidified into a crystalline white mass.  M.p. 83-85° 4.5 g of thiophene was
added to the resultant pyridine bissulfotrioxide, and the mixture was stirred
and allowed to stand at room temperature.  Ten hours later 17.5 g of phosphorus
pentachloride was added to the light-colored thick liquid, and the reaction
mixture was heated to 70-80° for 2 hours.  It was poured out over ice after it
had cooled, and the crystalline sulfochloride filtered out.  At room temperature
it turned into a paste, which crystallized after 2 days of standing, m.p. 28-
30°.  The m.p. of the sulfochloride was raised to 31-32° by recrystallization
from petroleum ether (b.p. 20-40°).  The mixed melting point when mixed with
the sulfochloride prepared by Method 1 exhibited no depression.

Thiophenesulfonamide was prepared by heating the sulfochloride with ammonium
carbonate and extracting with ether.  M.p. 144.5-146°.  The melting points given
in the literature are: 146-147° and 141° [8,5]..

   3.210 mg substance: 0.2400 ml $N_2$ (29°, 747 mm).  Found %: N 8.31. $C_4H_5O_2NS_2$.
   Calc. %: N 8.58.

Thiophenesulfanilide had a m.p. of 99.5-100° (from an aqueous-alcoholic
solution).  V. Meyer gives the m.p. as 96° [5].

   5.993 mg substance: 0.3185 ml $N_2$ (30°, 754 mm).  Found %: N 5.95. $C_{10}H_8O_2NS_2$.
   Calc. %: N 5.88.

## SUMMARY

It has been shown that reacting thiophene with pyridine sulfotrioxide at
20-30° produces thiophenesulfonic-2 acid (50% yield).  At a temperature of
95-100° the monosulfonation is paralleled by the formation of a disulfo acid.
The reagent is utilized nearly quantitatively at 130°, as well as when an
"acid" reagent is employed, yielding a mixture of the 2,4 and 2,5 isomers
of thiophenesulfonic acids.

It has been shown that pyridine yields a compound containing two $SO_3$ mole-
cules: pyridine bissulfotrioxide, a powerful sulfonating agent that can be
employed to sulfonate various acidophobic compounds.  It sulfonates thiophene
without any tarring at 20-30°, with an 86% yield of thiophenesulfonic-2 acid.

It has been shown that the primary products of sulfonation with pyridine
sulfotrioxide and pyridine bissulfotrioxide may be used instead of the
potassium salts to secure the acid chlorides of sulfonic acids.  This method
affords high yields.

## LITERATURE CITED

   [1]  A. P. Terentyev, Bull, Moscow State Univ. 6, 9, 62 (1947).

   [2]  A. P. Terentyev, and L. A. Kazitsina, Proc, USSR Acad. Sci. 55, 631
(1947); J. Gen. Chem. 18, 723 (1948); 19, 531* (1949).

   [3]  A. P. Terentyev, and G. M. Kadatsky, J. Gen. Chem. 21, 1524**(1951).

   [4]  A. P. Terentyev, and L. A. Yanovskaya, J. Gen. Chem. 19, 535;***1365
(1949).

   [5]  V. Meyer, Die Thiophengruppe,  p.  111-117 (1888);  Ann., 236, 206
(1866);  V. Meyer, H. Kreis, Ber., 16, 2173 (1883).

   [6]  L. Weitz, Ber., 17, 796 (1884).

   [7]  A. Tohl, Ber., 27, 665 (1894).

* See C.B. English translation, p.  481.
** See C.B. English translation, p. 1667.
*** See C.B. English translation, p. 487.

[8]  W. Steinkopf, T. Hopner, Ann., 501, 174 (1943)

[9]  V. Meyer, Op. cit. p. 131-135 (1888).

[10]  H. Jackel, Ber., 19, 185 (1885).

The N. D. Zelinsky laboratory of Organic Chemistry,
Moscow State University

## XVI. SYNTHESIS OF THE MESO DERIVATIVES OF ANTHRACENE, USING

## ORGANOLITHIUM COMPOUNDS

B. M. Mikhailov and V. P. Bronovitskaya

One of the present authors [1] has previously found that the reaction of
the meso derivatives of anthracene with n-butyllithium yields organolithium
compounds of anthracene, which may be used successfully for synthesis, as has
been illustrated in several instances. The present paper reports the results
of work on the development and improvement of the synthesis of anthracene
derivatives by means of organolithium compounds, as well as the elucidation
of various problems related to the exchange reactions of a halogen and lithium
in the anthracene series.

Basing ourselves on the experimental production of organolithium compounds
from 9-bromoanthracene and 9,10-dibromoanthracene, we first resorted to n-
butyllithium to secure an organolithium compound of 9-chloro-10-bromoanthracene.
The subsequent action of various reagents upon the resultant 9-chloroanthryl-
10-lithium gave us meso derivatives of 9-chloranthracene, but the product
yields did not exceed 35-50% in the best of cases, and were exceedingly small
in some instances. No more than 4.5% of the theoretical yield of 9-ethyl-10-
chloroanthracene was secured, for example, when we reacted ethyl iodide with
the lithium compound prepared from 9-chloro-10 bromoanthracene. These unsatis-
factory results are doubtless due, as B. M. Mikhailov and T. K. Kozminsky have
shown in the 1,2-benzanthracene series [2], to the fact that the n-butyl bromide
formed in the double decomposition reaction between 9-chloro-10-bromoanthracene
and n-butyllithium reacts, in turn, with the organolithium compound, thus
withdrawing the latter from the zone of subsequent transformations. It was
therefore likely that using phenyllithium instead of n-butyllithium would
prevent this secondary reaction, inasmuch as bromobenzene does not react with
organolithium compounds of the anthracene series. As a matter of fact, we
were able to secure much higher yields of 9-chloroanthracene derivatives by
synthesizing 9-chloroanthryl-10-lithium with phenyllithium and then reacting
it with various reagents, than we had ever secured in our experiments in which
n-butyllithium was used.

When we reacted 9-chloroanthryl-10-lithium with carbon dioxide, for example,
we secured a 73% yield of 9-chloroanthracene-10-carboxylic acid (I, R = COOH)
instead of the 36% yield when n-butyllithium was used, and reacting the product
with methyl iodide yielded 88% of 9-methyl-10-chloroanthracene (I, R = $CH_3$),

195

whereas only 50% was secured when n-butyllithium was used, while the yield of 9-ethyl-10-chloroanthracene (I, R = $C_2H_5$) was similarly raised from 4.5 to 47%.



$$n-C_4H_9Li \text{ or } C_6H_5Li$$

(I)

R = COOH, $CH_3$, $C_2H_5$
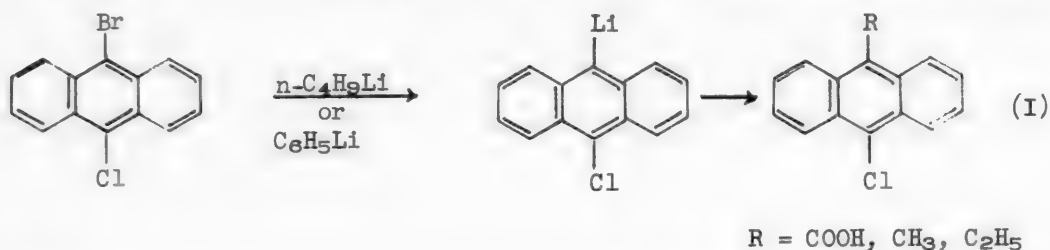
We found that the substitution of one atom of lithium for one atom of bromine took place no less smoothly when one equivalent of phenyllithium was reacted with 9,10-dibromoanthracene. Carboxylating the reaction products produced a 91% yield of 9-bromoanthracene-10-carboxylic acid (II, R = COOH), which was converted into 9-methyl-10-bromoanthracene (II, R = $CH_3$) by the action of methyl iodide, with a yield of 76%, and into 9-ethyl-10-bromoanthracene (II, R = $C_2H_5$) by the action of ethyl iodide.



(II)

R = COOH, $CH_3$, $C_2H_5$
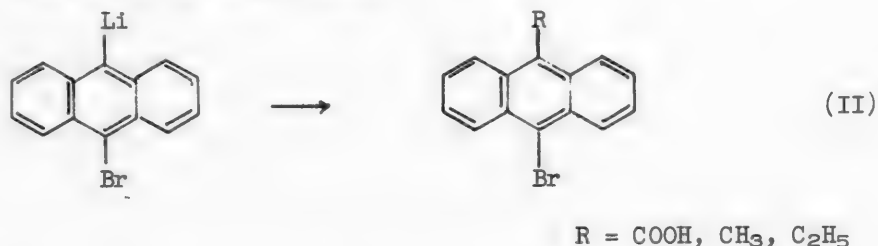
Reacting 9-methyl-10-bromoanthracene with phenyllithium yielded 9-methyl-anthryl-10-lithium, which was converted into 9-methylanthracene-10-carboxylic acid (III, R = COOH) by the action of carbonic acid, and into 9-methyl-10-ethylanthracene (III, R = $C_2H_5$) by the action of ethyl iodide. The action of methyl iodide upon the lithium compound of 9-methylanthracene, prepared with n-butyllithium, yielded 9,10-dimethylanthracene (III, R = $CH_3$).



(III)

R = $CH_3$, $C_2H_5$, COOH
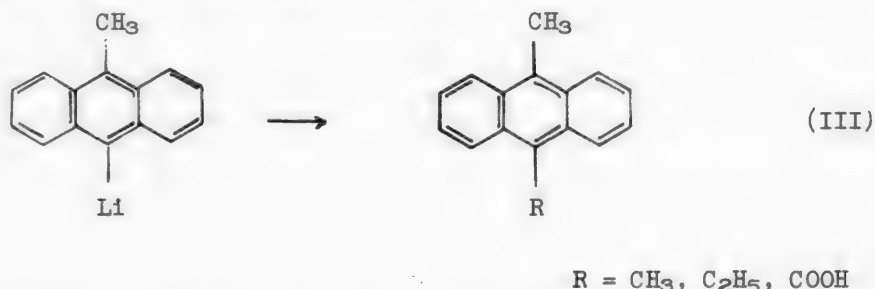
We then investigated the ability of the two bromine atoms in 9,10-dibromo-anthracene to be replaced by lithium. Reacting 2 equivalents of n-butyllithium with 9,10-dibromoanthracene and then reacting the resulting organolithium compound with methyl iodide yielded about 40% of rather impure 9,10-dimethylanthracene, which was hard to purify, so that yield of the pure preparation did not exceed 16%; about 13% of the theoretical yield of 9,10-di- β -hydroxyethylanthracene (IV) was secured by reacting the reaction products with ethylene oxide.

$CH_2 - CH_2OH$
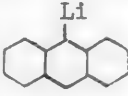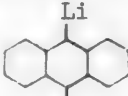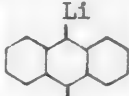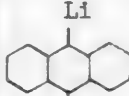
(anthracene ring structure)

$CH_2 - CH_2OH$
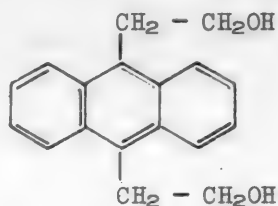
(IV)

The substitution of lithium for the second bromine atom in 9,10-dibromo-anthracene requires fewer steps when 2 equivalents of phenyllithium are used. When the process was carried out for one hour at 50°, for example, and the reaction products then carboxylated, we secured 82% of the theoretical yield of 9-bromoanthracene-10-carboxylic acid, only 8% of the bromide being converted into the 9,10-dicarboxylic acid of anthracene; this proportion remained about the same when the reaction between the bromide and phenyl-lithium was carried out for 3 hours at 50°.

In contrast to the bromine derivatives, the chloride derivatives of anthracene do not enter into an exchange reaction of lithium for the halogen when they are reacted with phenyllithium. When 9-chloroanthracene was heated to 40° for 2 hours with 2 equivalents of phenyllithium, for instance, and the reaction mixture was then reacted with carbon dioxide, no anthracene-10-carboxylic acid was secured at all, while reacting 9-chloro-10-bromoanthracene with 2 equivalents of phenyl-lithium for 15 minutes, followed by carboxylation of the reaction products yielded nothing but 9-chloroanthracene-10-carboxylic acid.

The apparent instability of the organolithium compounds of anthracene secured when n-butyllithium is used, manifested in the decrease of the percentage of these compounds in the reaction mixture as the length of exposure to the reagents is increased (Table 1), was borne out by experiments on the reaction of bromine derivatives of anthracene with metallic lithium [1] in ether, in which organolithium compounds were either not produced at all or else produced with very poor yields, the principal reaction product being a hydrocarbon. Tests we ran in which the length of time the anthracene bromo derivatives were reacted with phenyllithium was varied indicated beyond any doubt, however, that the organolithium compounds of anthracene were stable in diethyl ether. We see in Table 1 that even two hours of heating at 40° has very little effect upon the percentage of organolithium compounds in the reaction mass.

TABLE 1[*]

| RLi | Time, Minutes | Temperature | Li (anthracene) %% | Li / Cl %% | Li / Br %% | Li / CH3 %% |
|---|---|---|---|---|---|---|
| n-C$_4$H$_9$Li | 5 | 15° | 77 | - | 58 | - |
| n-C$_4$H$_9$Li | 15 | 40 | 58 | 36 | 80 | - |
| n-C$_4$H$_9$Li | 120 | 40 | 44 | - | 37 | - |
| C$_6$H$_5$Li | 15 | 15 | - | 73 | 91.3 | 13.8 |
| C$_6$H$_5$Li | 120 | 15 | 63.6 | - | - | 62.8 |
| C$_6$H$_5$Li | 120 | 40 | 71.7 | 69 | 88.3 | 62.8 |
| C$_6$H$_5$Li | 300 | 40 | - | - | 86 | - |

[*]See footnote on next page.

It is therefore obvious that the formation of hydrocarbons when bromine derivatives of anthracene are reacted with metallic lithium [1], such as the formation of anthracene from 9-bromoanthracene and lithium, is not due to the instability of the organolithium compounds in ether, but is caused by some unknown course of the reaction, which requires further study.

## EXPERIMENTAL**

9-Chloroanthracene-10-carboxylic acid. 1 g of 9-chloroanthracene-10-bromoanthracene (m.p. 210.5-211°) [3] was added to a solution of phenyllithium, prepared in an ampoule from 0.9 g of bromobenzene, 0.09 g of lithium, and 5 ml of ether. The ampoule was carefully agitated at room temperature for 15 minutes, and then the brownish-yellow solution of the organometallic compound was poured over dry ice. Ether and water were added to the reaction products. The acid that settled out when the aqueous layer was acidulated was crystallized from alcohol. This yielded 0.64 g of the acid (73% of the theoretical) with a m.p. of 262-264°. After recrystallization from the same solvent, the substance consisted a yellow needles with a m.p. of 268.5-269.5°.

5.455 mg substance: 14.044 mg $CO_2$; 1.853 mg $H_2O$. Found %: C 70.38; H 3.80. $C_{15}H_{19}O_2Cl$. Calc. %: C. 70.18; H 5.53.

In an experiment in which n-butyllithium was used, 36% of the theoretical yield of an acid with a m.p. of 265-267° was secured after the reagents had interacted for 10 minutes and the reaction products had then been carboxylated.

9-Ethyl-10-chloroanthracene. An ether solution of 2.6 g of ethyl iodide was added to 10-chloroanthryl-9-lithium, prepared with phenyllithium as outlined above, and the reaction mixture was heated to 50° in a sealed ampoule for 3 hours. When heating was complete, the ether solution was washed with water, and the solvent was driven off. After being twice recrystallized from methanol, followed by crystallization from alcohol and then from acetone, the residue had a m.p. of 107-109° (0.39 g, or 47% of the theoretical). After another recrystallization from acetone the substance consisted of yellow leaflets with a m.p. of 109-110°. The m.p. of 9-ethyl-10-chloroanthracene is given in the literature as 111° [4]. When n-butyllithium was used, 4.5% of the theoretical yield of 9-ethyl-10-chloranthracene (m.p. 105-109°) was secured.

9-Methyl-10-chloroanthracene. An ether solution of 1.5 g of methyl iodide was added to 10-chloroanthryl-9-lithium, prepared similarly from the same quantities of reagents as specified above. Considerable heat was evolved, and a yellow precipitate was thrown down. The reaction mass was washed with water, the crystalline precipitate filtered out (0.54 g, m.p. 173-179°), the ether layer evaporated, and the residue crystallized from alcohol. This yielded 0.14 g of a substance with a m.p. of 173-179°. The total yield of 9-methyl-10-chloro-anthracene was 0.68 g, or 88% of the theoretical. After recrystallization from a benzene - alcohol mixture, the 0.56 g of the substance had a m.p. of 179-180°. The 9-methyl-10-chloranthracene we had synthesized by reacting 9-methylanthracene with phosphorus pentachloride had a m.p. of 179-180° [3]. The yield of 9-methyl-10-chloranthracene (m.p. 174-177°) was 50% of the theoretical when n-butyllithium was used.

---

*The percentage of organolithium compounds in the reaction mixture was estimated from the yields of carboxylic acids secured when the reaction products were reacted with carbon dioxide.

**All operations with organolithium compounds were performed in an atmosphere of nitrogen.

9-Bromoanthracene-10-carboxylic acid. 2 g of 9,10-dibromoanthracene was added to a phenyllithium solution prepared in an ampoule with 1.8 g of bromobenzene, 0.18 g of lithium, and 10 ml of ether. The mixture was agitated for 15 minutes at room temperature, and then the yellow-brown solution of the organometallic compound was poured over dry ice. Ether and water were added to the reaction products. Aciduating the aqueous layer yielded 1.65 g of an acid with a m.p. of 259-262° (91.3%). After the acid had been recrystallized from a benzene-alcohol mixture, it consisted of yellow needles with a m.p. of 265-267° (1.32 g) [1].

9-Methyl-10-bromoanthracene. 5 g of methyl iodide, diluted with ether, was added to 10-bromoanthryl-10-lithium, prepared as outlined above from 4 g of 9,10-dibromoanthracene and phenyllithium. Considerable heat was evolved, and a yellow precipitate was thrown down. The reaction mass was washed with water, and the crystalline precipitate was filtered out and crystallized from a benzene-alcohol mixture. This yielded 2.37 g of 9-methyl-10-bromoanthracene, m.p. 170-173°. The ether solution was evaporated, and the residue was recrystallized twice from a benzene-alcohol mixture. This yielded another 0.11 g of the bromide, m.p. 169-173°. The yield was 76% of the theoretical. The bromide had a melting point of 172-173° after the second recrystallization. A yield of 42.5% of the bromide was secured by reacting 9-methylanthracene with phosphorus pentachloride [3].

9-Ethyl-10-bromoanthracene. An ether solution of 2.8 g of ethyl iodide was added to 10-bromoanthracene-9-lithium, prepared with 2 g of 9,10-dibromoanthracene and phenyllithium. The ampoule was then sealed and heated to 50° for 3 hours. Then the reaction mass was washed with water, and the residue left after the solvent had been driven off was processed with several portions of a benzene-alcohol mixture. This yielded 0.63 g (37% of the theoretical) of a substance with a m.p. of 109-110° in the form of yellow needles. The literature gives the m.p. of 9-ethyl-10-bromoanthracene as 104° [5].

9,10-Dimethylanthracene. a) From 9,10-dibromoanthracene. 0.7 g of 9,10-dibromoanthracene was added to a n-butyllithium solution prepared with 0.6 g of n-butyl chloride, 0.08 g of lithium, and 10 ml of ether. Considerable heat was evolved and a dark-yellow precipitate of an organolithium compound was thrown down. The ampoule was carefully shaken for 15 minutes at room temperature, and then an ether solution of 1.8 g of methyl iodide was added. The reaction was accompanied by foaming and the precipitation of a light-yellow deposit. Half an hour later the reaction products were washed with water, the ether solution evaporated, and the residue crystallized from alcohol. This yielded 0.17 g of a substance with a m.p. of 162-175°. Recrystallization from a benzene-alcohol mixture yielded 0.07 g (16% of the theoretical) of a hydrocarbon with a m.p. of 183.5-184.5° as lustrous yellow needles that exhibited no depression of the melting point when mixed with a sample of 9,10-dimethylanthracene [6].

b) From 9-methyl-10-bromoanthracene. 0.5 g of 9-methyl-10-bromoanthracene (m.p. 172-173°) was added to a solution of n-butyllithium, prepared with 0.26 g of n-butyl chloride, 0.05 g of lithium, and 10 ml of ether. The reaction mixture was gently shaken at room temperature for 15 minutes, and then an ether solution of 0.8 g of methyl iodide was added. Some heat was evolved, and a crystalline yellow precipitate was thrown down. One hour later the reaction products were washed with water, the precipitate filtered out, and the ether solution evaporated. The residue was combined with the

crystalline precipitate and crystallized from a benzene-alcohol mixture. This yielded 0.25 g of a substance with a m.p. of 171-181.5°. Another recrystallization from a benzene-alcohol mixture yielded 0.2 g of a hydrocarbon (52.6% of the theoretical) with a m.p. of 183.5-184.5°.

9,10-Di-β-hydroxyethylanthracene. 0.7 g of 9,10-dibromoanthracene was added to a solution of n-butyllithium, prepared with 0.6 g of n-butyl chloride, 0.08 g of lithium, and 10 ml of ether. The ampoule was shaken for 15 minutes, and then gaseous ethylene oxide was passed through the reaction mass, the solution growing lighter and a voluminous yellow precipitate being thrown down. When the reaction was over, the alcoholate was decomposed with water, the precipitate (0.1 g with a m.p. of 210-215°) being filtered out, and the ether solution being evaporated to small volume. Another 0.03 g of a substance with a m.p. of 209-215° was recovered from the concentrated ether solution. Recrystallization of the combined precipitates from alcohol yielded 0.07 g (12.8% of the theoretical) of a substance as yellow needles with a m.p. of 220-223°. A second recrystallization from alcohol raised the substance's m.p. to 223.5-224.5°.

3.469 mg subs.: 10.350 mg $CO_2$; 2.224 mg $H_2O$. Found %: C 81.42; H 7.17. $C_{18}H_{18}O_2$. Calc. %: C 81.17; H 6.81.

9-Methylanthracene-10-carboxylic acid. 0.54 g of 9-methyl-10-bromoanthracene was added to a solution of n-butyllithium, prepared with 0.26 g of n-butyl chloride, 0.05 g of lithium, and 10 ml of ether. The reaction mixture was carefully shaken for 10 minutes at room temperature and then poured over dry ice. Ether and water were added to the reaction products, and the aqueous layer was separated and acidified. The precipitated acid (0.3 g, m.p. 203-206°) was crystallized from dilute alcohol. This yielded 0.2 g (42.5% of the theoretical) of the acid as lustrous yellow leaflets with a m.p. of 211-217°. Recrystallization of the acid from alcohol raised its m.p. to 219-220°.

3.406 mg subs.: 10.122 mg $CO_2$; 1.654 mg $H_2O$. Found %: C 81.10; H 5.43. $C_{16}H_{12}O_2$. Calc. %: C 81.33; H 5.12.

The same yield of 9-methyl-10-anthracenecarboxylic acid was secured by using phenyllithium, but in this experiment the mixture of 9-methyl-10-bromoanthracene was kept at room temperature for 1.5 hours.

9-Methyl-10-ethylanthracene. 1 g of 9-methyl-10-bromoanthracene was added to a solution of phenyllithium, prepared with 0.96 g of bromobenzene, 0.18 g of lithium, and 10 ml of ether. The ampoule was kept at room temperature, with stirring at intervals, for 2.5 hours, after which an ether solution of 1.75 g of ethyl iodide was added, and the ampoule was sealed and heated to 50° for 3 hours. The reaction products were washed with water, the ether solution evaporated, and the residue crystallized from alcohol. This yielded 0.54 g of a substance with a m.p. of 128-136°. Recrystallization from a benzene-methanol mixture yielded 0.46 g (57% of the theoretical) of a hydrocarbon with a m.p. of 139-141°. Still another recrystallization from the same solvents raised the m.p. of the substance to 142-144°. The literature gives the melting point of 9-methyl-10-ethylanthracene as 143-144° [7].

## SUMMARY

1. A study has been made of the reactions of the meso halogen derivatives of anthracene with n-butyllithium and phenyllithium, which result in the formation of organolithium compounds of anthracene. It is advisable to use phenyl-

lithium in synthesizing these compounds, since its use eliminates the side reactions that take place when n-butyllithium is employed.

2. The organolithium compounds have been employed in the synthesis of various meso derivatives of anthracene.

3. The extent of the substitution of lithium for the two bromine atoms in the dibromo derivatives of anthracene is negligible when an excess of phenyllithium is used.

4. The meso chloro derivatives of anthracene do not react with phenyl-lithium.

5. The organolithium compounds of anthracene are fairly stable in an ether medium.

## LITERATURE CITED

[1]  B. M. Mikhailov, Bull. Acad. Sci. USSR Div. Chem. Sci. 1948, 4, 420.

[2]  B. M. Mikhailov and T. K. Kozminskaya, J. Gen. Chem. 21, 1276[*](1951).

[3]  B. M. Mikhailov and M. Sh. Promyslov, J. Gen. Chem. 20[**], 338 (1950).

[4]  Krollpfeifer and Brandscheid, Ber., 56, 1618 (1923).

[5]  B. Barnett and M. Mathews, Ber., 59, 1429 (1926).

[6]  B. M. Mikhailov, Bull. Acad. Sci. USSR Div. Chem. Sci. 1946, 6, 619, (1946).

[7]  A. Willemart, Bull. Soc. chim., [5], 5, 556 (1938).

[*]See C.B. English translation, p. 1395.
[**] See C.B. English translation, p. 359.

I.   ADDITION OF ALKALI METALS TO 1,2,3,4-TETRAHYDRONAPHTHACENE.

TRANSFORMATIONS OF THE BIMETALLIC COMPOUNDS OF
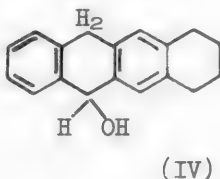
1,2,3,4-TETRAHYDRONAPHTHACENE

B. M. Mikhailov and A. D. Chinaeva

In synthesizing the derivatives of 1,2,3,4-tetrahydronaphthacene we used a method based upon the transformations of organometallic compounds produced by directly adding alkali metals to polycyclic compounds [1].

The initial hydrocarbon 1,2,3,4-tetrahydronaphthacene (III) was synthesized, with a 79% yield, from the readily available 1,2,3,4-tetrahydronaphthacenequinone (I) [2]. The quinone was first reduced by stannous chloride and hydrochloric acid to 1,2,3,4-tetrahydronaphthacenone 6 (II), which was then reduced with zinc dust and an alkali to the hydrocarbon.



(I)                        (II)                        (III)
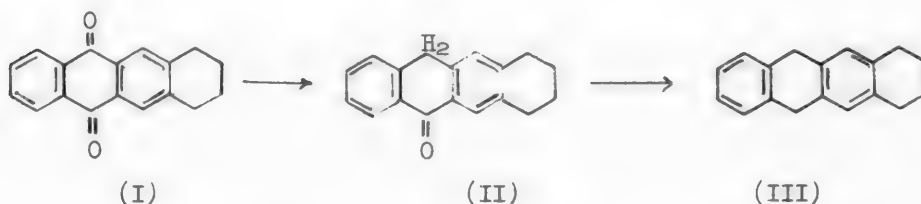
A by-product in the synthesis of the hydrocarbon (III) was a minute quantity of 1,2,3,4,6,11-hexahydronaphthacenol-6 (IV), m.p. 174-175°.



(IV)

The compound (IV) loses a molecule of water and is converted into 1,2,3,4--tetrahydronaphthacene (III) when it is heated to about 200° or boiled in a mixture of acetic anhydride and acetic acid, the yield of the hydrocarbon amounting to some 55% when the latter method is employed.

Braun, Bayer, and Fieser [3] previously secured a 10% yield of 1,2,3,4-tetra-

-hydronaphthacene (III) by reducing 1,2,3,4-tetrahydronaphthacenequinone cata-
lytically, as well as by dehydrating the product (with an unsharp melting point
of about 120°) secured by reducing the quinone (I) with zinc dust in the presence
of ammonia and potassium hydroxide (though the yield was not given). The authors
attribute the structure of 1,2,3,4,6,11-hexahydronaphthacenol-6 to the reduction
product of the quinone (I), though our findings indicate that this substance's
melting point is 174-175° rather than roughly 120°.

A study of the addition of alkali metals to 1,2,3,4-tetrahydronaphthacene
has shown that sodium and lithium are added rather quickly to the hydrocarbon
in ether, and even more rapidly in ethylene glycol dimethyl ether. The solution
of the resulting organosodium compound of tetrahydronaphthacene is dark green
whether the first or second ether is used as the medium. The action of methanol
upon the organosodium compound (V) yielded 1,2,3,4,6,11-hexahydronaphthacene (VI)
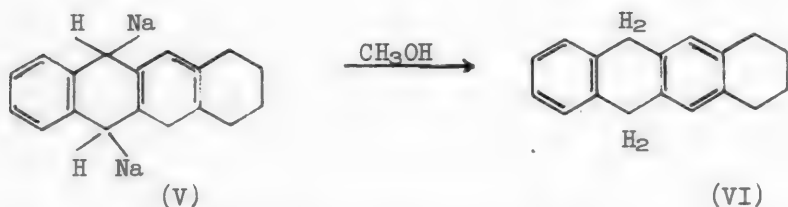


When lithium is added to tetrahydronaphthacene in ether, the solution is
colored violet, its color being dark green when ethylene glycol dimethyl ether
is employed. The metal is not added to the hydrocarbon all at once, addition
occurring only after the reaction mixture is agitated for 6 to 9 hours. Once
it has set in, however, the reaction is rapid, ending after 3 hours in ethylene
glycol dimethyl ether. The action of carbon dioxide upon the dilithium compound
of tetrahydronaphthacene (VII) produces a mixture of geometrical isomers of
1,2,3,4,6,11-hexahydronaphthacene-6,11-dicarboxylic acid (VIII), from which one
of the isomers (cis or trans), with a m.p. of 198-204° (with decomposition), was
isolated.

In the course of our research we found that the organolithium compound (VII)
was unstable in ethylene glycol dimethyl ether, being partially hydrolyzed to
1,2,3,4,6,11-hexahydronaphthacyl-6-lithium (IX) when coming into contact with
it. When the addition of the metal to the hydrocarbon was prolonged to 10 hours
(from the onset of the reaction), the following carboxylation of the reaction
products yielded 1,2,3,4,6,11-hexahydronaphthacene-6-carboxylic acid (X) in
addition to the 1,2,3,4,6,11-hexahydronaphthacene-6,11-dicarboxylic acid.

H Li      $\xrightarrow{CO_2}$      H COOH

H$_2$       (IX)            H$_2$     (X)
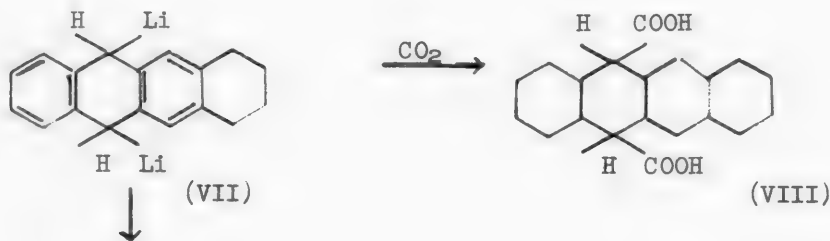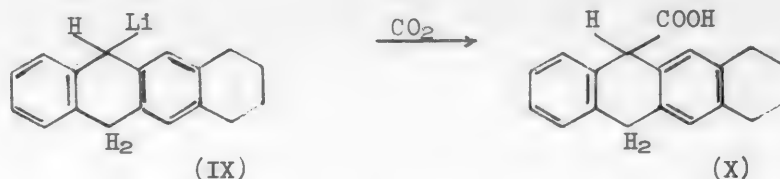
The action of methyl chloride upon the dilithum compound (VII) yields a mixture of the geometrical isomers of 6,11-dimethyl-1,2,3,4,6,11-hexahydronaphthacene (XI), the cis and trans isomers of which were isolated in the pure state.



H CH$_3$

H CH$_3$      (XI)
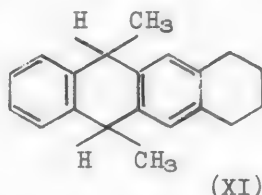
Oxidation of the mixture of cis and trans isomers (XI) yielded 1,2,3,4-tetrahydronaphthacenequinone, which located the position of the methyl groups in the molecule.

### EXPERIMENTAL

1,2,3,4-Tetrahydronaphthacene (III). A mixture consisting of 10 g of 1,2,3,4-tetrahydronaphthacenequinone (m.p. 216-217°) [2], 30 g of stannous chloride, 60 ml of concentrated hydrochloric acid, and 220 ml of glacial acetic acid was boiled for an hour, after which the brown-red reaction mixture was poured into cold water.

The light-yellow precipitate was filtered out and washed with water. The synthesized 1,2,3,4-tetrahydronaphthacenol had a m.p. of 140-142° without recrystallization. Then the wet precipitate was mixed with 20 g of zinc dust and 200 ml of 2N aqueous potassium hydroxide solution, and the mixture was boiled for 3 hours. The brown reaction mixture was quickly cooled, the resulting precipitate being filtered out and treated with 10% hydrochloric acid to remove the excess zinc dust. Then the substance was washed with water, dried, and crystallized from chloroform. This yielded 6.9 g of 1,2,3,4-tetra--hydronaphthacene as green-yellow leaflets with a m.p. of 243-244°. The yield was 77.9% of the theoretical. Fieser [3] gives the m.p. of 1,2,3,4-tetrahydro--naphthacene as 233°.

4.792 mg subs.: 16.323 mg $CO_2$; 3.053 mg $H_2O$. Found %: C 92.95; H 7.12. $C_{18}H_{16}$. Calc. %: C 93.06; H 6.94.

Adding methyl alcohol to the chloroform filtrate yielded 0.82 g of a substance with a m.p. of 173-175° and 0.34 g with a m.p. of 164-173°. Dehydration of these fractions with acetic anhydride and acetic acid (see below) yielded another 0.09 g of 1,2,3,4-tetrahydronaphthacene. The total yield of 1,2,3,4-tetrahydronaphthacene was 79%.

1,2,3,4,6,11-Hexahydronaphthacenol-6 (IV). The by-product with a m.p. of

173-175° that was isolated during the synthesis of 1,2,3,4-tetrahydronaphthacene was crystallized from chloroform and then from benzene. This yielded a substance in the shape of colorless needles with a m.p. of 174-175°.

6.065 mg subs.: 19.260 mg $CO_2$; 3.779 mg $H_2O$. Found %: C 86.66; H 6.97. $C_{18}H_{18}O$. Calc. %: C 86.36; H 7.24.

The substance was soluble in benzene and chloroform, and sparingly soluble in alcohol, acetone, and ether.

Dehydration of 1,2,3,4,6,11-hexahydronaphthacenol-6. A mixture of 1 g of 1,2,3,4,6,11-hexahydronaphthacenol-6, 23 ml of acetic anhydride, and 2 ml of glacial acetic acid was refluxed for 3 hours. When the reaction solution cooled, a crystalline substance with a m.p. of 238-240° was precipitated; it exhibited no depression with 1,2,3,4-tetrahydronaphthacene. The yield was 0.52 g, or 55.4% of the theoretical.

1,2,3,4,6,11-Hexahydronaphthacene (VI). A mixture of 0.2 g of 1,2,3,4-tetrahydronaphthacene, 0.056 g of sodium, and 5 ml of ethylene glycol dimethyl ether was placed in an ampoule, the air was driven off with nitrogen, and the ampoule was sealed and agitated for 12 hours. Then 2 ml of methanol diluted with 5 ml of ether was carefully added to the dark-green reaction mixture. The precipitate constituted the unreacted initial hydrocarbon. The colorless filtrate was diluted with water, the substance thrown down being filtered out (0.11 g) and recyrstallized twice from a benzene-alcohol mixture. M.p. 127-128°. The literature gives the m.p. of 1,2,3,4,6,11-hexahydronaphthacene as 128° [3].

1,2,3,4,6,11-Hexahydronaphthacene-6,11-dicarboxylic acid (VIII). 0.06 g of lithium, 0.5 g of 1,2,3,4-tetrahydronaphthacene, and 5 ml of ethylene glycol dimethyl ether were placed in a bottle filled with nitrogen. The reaction set in after 6 hours of agitation at room temperature, the mixture becoming dark-green and then turning to brown-red. The reaction mixture was agitated for 3 more hours after the color first appeared. Dry ice was added to the resulting organometallic compound, and then the carboxylation products were dissolved in water. The insoluble precipitate (40 mg) was filtered out, and the solution was acidulated with 10% hydrochloric acid. The resulting mixture of the cis and trans isomers of 1,2,3,4,6,11-hexahydronaphthacene-6,11-dicarboxylic acid was reprecipitated and dried in a vacuum desiccator. This yielded 0.42 g of acids with a m.p. of 162-176° (60.1% of the theoretical).

3.532 mg subs.: 9.650 mg $CO_2$; 1.964 mg $H_2O$. Found %: C 74.56; H 6.22. $C_{20}H_{18}O_4$. Calc. %: C 74.52; H 5.63.

Repeated recrystallization of the acid mixture from dilute alcohol isolated one of the cis-trans isomers of 1,2,3,4,6,11-hexahydronaphthacene-6,11-dicarboxylic acid as minute colorless needles with a m.p. of 198-204° (with decomposition).

3.522 mg subs.: 9.621 mg $CO_2$; 2.003 mg $H_2O$. Found %: C 74.54; H 6.36. $C_{20}H_{18}O_4$. Calc. %: C 74.52; H 5.63.

1,2,3,4,6,11-Hexahydronaphthacene-6-carboxylic acid (X). Ten hours of agitation after the onset of the reaction of the same quantities of substances, under the same conditions, as those described in the preceding experiment, yielded 0.49 g of a mixture of acids consisting of the cis-trans isomers of 1,2,3,4,6,11-hexahydronaphthacene-6,11-dicarboxylic acid and 1,2,3,4,6,11-hexahydronaphthacene-6-carboxylic acid, with a m.p. of 92-115°.

3.533 mg subs.: 10.296 mg $CO_2$; 2.141 mg $H_2O$. Found %: C 78.99; H 6.78. $C_{18}H_{18}O_2$. Calc. %: C 81.98; H 6.52; $C_{20}H_{18}O_4$. Calc. %: C 74.52; H 5.63.

Recrystallization of the mixture from alcohol and then from acetic acid yielded tetrahedral platelets of 1,2,3,4,6,11-hexahydronaphthacene-6-carboxylic acid with a m.p. of 187-196° (with decomposition).

3.841 mg subs.: 11.488 mg $CO_2$; 2.232 mg $H_2O$. Found %: C 81.62; H 6.53. $C_{19}H_{18}O_2$. Calc. %: C 81.98; H 6.52.

6,11-Dimethyl-1,2,3,4,6,11-hexahydronaphthacene (XI). 2 g of 1,2,3,4--tetrahydronaphthacene, 0.24 g of lithium, and 20 ml of ethylene glycol dimethyl ether were charged into a bottle filled with nitrogen. The reaction set in after the bottle had been agitated for 6 hours, agitation being continued for another 3 hours after that. Then the reaction bottle was connected to a two-tube adapter, one end of which was terminated by a calcium chloride tube, while the other was fitted with a glass tube extending to the bottom of the bottle, through which a current of anhydrous methyl chloride was passed. As the gas passed through the solution, the color of the organolithium compound disappeared, and lithium chloride was precipitated. When the reaction was over, the solvent was driven off, and the residue was extracted with benzene. The benzene solution was washed with water, the solvent driven off, and the 2.15 g of residue, a fluorescent yellow oil, was dissolved in alcohol. Within 24 hours 0.98 g of a crystalline substance with a m.p. of 87-135° was filtered out of the alcoholic solution. Another 0.34 g of a substance with a m.p. of 78-91° crystallized out of the filtrate after it had stood for some more time. The resultant fractions were dissolved in chloroform, 13 mg of the initial 1,2,3,4-tetrahydronaphthacene being recovered from the chilled solution. Adding acetone to the chloroform filtrate crystallized a colorless crystalline substance, the m.p. of which was 150.5-151° after recrystallization from alcohol, an acetone-alcohol mixture, and lastly ethyl acetate. Analysis indicated that this substance was the trans(cis) isomer of 6,11-dimethyl-1,2,3,4,6,11-hexahydronaphthacene.

4.215 mg subs.: 14.121 mg $CO_2$; 1.708 mg $H_2O$. Found %: C 91.42; H 8.37. $C_{20}H_{22}$. Calc. %: C 91.54; H 8.45.

The hydrocarbon crystallized from acetone as colorless hexagonal platelets. It was freely soluble in benzene and chloroform, less so in acetone, alcohol, ethyl acetate, and methanol.

Repeated recrystallization of the crystalline fractions left after the isolation of the isomer of 6,11-dimethyl-1,2,3,4,6,11-hexahydronaphthacene with a m.p. of 150.5-151°, first from acetone, then from an acetone-alcohol mixture, then from ethyl acetate, and finally from alcohol, yielded a substance as colorless needles with a m.p. of 125-126', which proved to be another (cis or trans) isomer of 6,11-dimethyl-1,2,3,4,6,11-hexahydronaphthacene upon analysis.

3.920 mg subs.: 9.776 mg $CO_2$; 2.332 mg $H_2O$. Found %: C 91.30; H 8.72. $C_{20}H_{22}$. Calc. %: C 91.54; H 8.45.

Oxidation of 6,11-dimethyl-1,2,3,4,6,11-hexahydronaphthacene. 0.1 g of a mixture of the cis and trans isomers of 6,11-dimethyl-1,2,3,4,6,11-hexahydronaphthacene, with a m.p. of 114-121°, was dissolved by heating it in 1 ml of glacial acetic acid, and 0.2563 g of chromic anhydride dissolved in acetic acid was added drop by drop to the boiling solution. The solution foamed violently. Then the reaction mixture was allowed to stand at room temperature for 15 hours. The precipitate was filtered out and washed with ether. The resulting substance had a m.p. of 216-217° and exhibited no depression of the melting point when mixed with a sample of the 1,2,3,4-tetrahydronaphthacenequinone synthesized earlier.

## SUMMARY

1.   Lithium and sodium are added to 1,2,3,4-tetrahydronaphthacene in ether or in ethylene glycol dimethyl ether.

2.   The organolithium compound of 1,2,3,4-tetrahydronapthacene is hydrolyzed to a monolithium compound by ethylene glycol dimethyl ether.

3.   The action of carbon dioxide or methyl chloride upon the dilithium compound of 1,2,3,4-tetrahydronaphthacene yields, respectively, 1,2,3,4,6,11-hexa--hydronaphthacene-6,11-dicarboxylic acid and the cis and trans isomers of 6,11--dimethyl-1,2,3,4,6,11-hexahydronaphthacene.

## LITERATURE CITED

[1]   B. M. Mikhailov, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1946, 619.

[2]   G. Schroeter, Ber., 54, 2242 (1921).

[3]   J. Braun, Bayer, Fieser, Ann., 459, 287 (1927).

# MEROCYANIN DYES THAT ARE DERIVATIVES OF RHODANINE

## II. THE PROPERTIES OF DIMETHENYLMEROCYANINS WITH VARIOUS NITROGEN-CONTAINING HETEROCYCLIC RESIDUES

M. V. Deichmeister, Z. P. Sytnik, and E. B. Lifshits.

The dimethenylmerocyanins – derivatives of rhodanine (Ia and Ib) – are rather efficient optical sensitizers of silver halide photographic emulsions [1].



(1b)
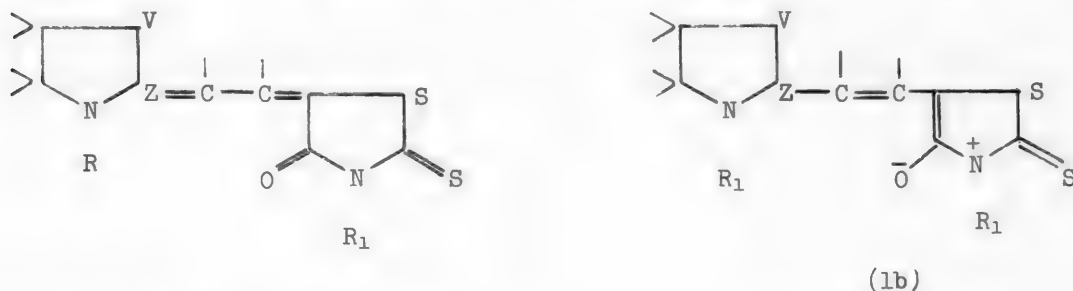
where R and $R_1$ are alkylis, aryls, or aralkyls; V is O, S, Se, $-CH=CH-$, $- C(CH_3)_2$, $=N-CH_3$, and so forth; and Z is carbon or the group $-CH=CH-C=$ (in the last instance there is no V group).

The patent literature [2] contains a large number of descriptions of such dyes and indicates the feasibility of using them as optical sensitizers for various regions of the spectrum. There is no information at all, however, on the variation of the photographic properties of these dyes with their structure, while the only reference to optical properties are a few comparisons made in Brooker's survey article [3]. The study of the optical and photographic properties of these merocyanins is of interest practically, as well as from the standpoint of the theoretical analysis of the color of inner ionoid compounds.

In the present paper we have explored the optical and photographic properties of the dimethenylmerocyanins – rhodanine derivatives – that differ in the nature of the nitrogen-containing heterocycle group. We have synthesized dyes of this type – derivatives of rhodanine and of its 3-ethyl derivatives – with the following groups containing an ethyl group attached to the nitrogen atom: 3,3-dimethylindolenine, thiazole, thiazoline, benzoxazole, β-naphthoxazole, benzothiazole, α-and β-naphtho--thiazoles, quinoline-(2 and 4), benzoselenazole, 5-methylthiodiazole-(1,3,4), pyridine-(2), and 1-methylbenzimidazole. We also synthesized monomethenyloxanines – derivatives of rhodanine and 3-ethylrhodanine (II).
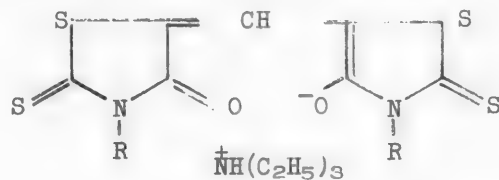


where R is H or $C_2H_5$

Most of the foregoing merocyanins were synthesized by reacting the 5-(acet-anilinomethylene)-rhodanines (III) with quaternary salts of the 2-methyl deri-vatives of the corresponding nitrogen-containing heterocyclic bases.

(III)

(IV)
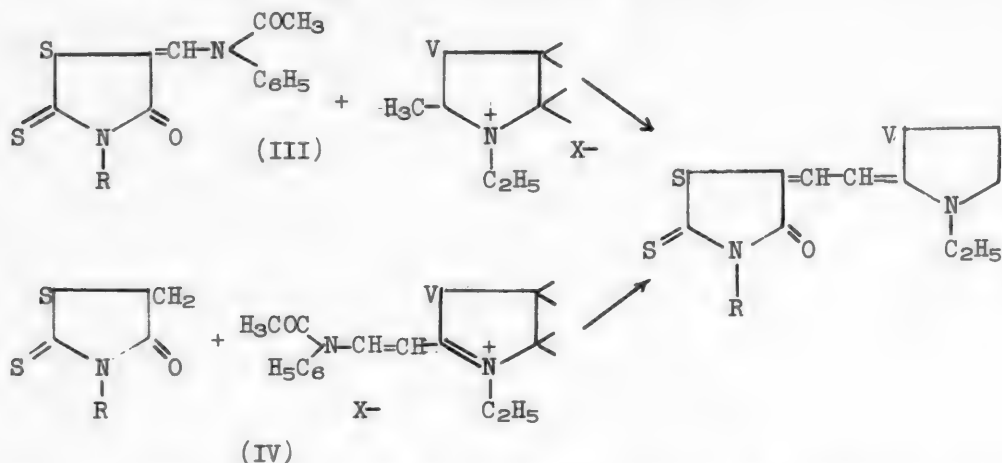
where R is H or $C_2H_5$; V is O, S, Se, $-CH=CH-$, $-C(CH_3)_2$ or $=N-CH_3$; and X is an acid radical.

We were either unable to synthesize some dyes [the derivatives of pyridine-(2), the benzoxazoles, and the napththoxazoles] in this way, or else their yields were very low [the derivatives of 5-methylthiodiazole-(1,3,4), thiazoline, and quinoline-(2)]. These compounds were synthesized by condensing quaternary salts of the acetanilinovinyl derivatives of the heterocyclic bases (IV) with rhodanine or 3-ethylrhodanine [4]. The oxanine dyes (II) were synthesized by condensing the respective acetanilinomethylene derivatives with rhodanine or 3-ethylrhoda-nine in pyridine containing triethylamine [5].

If the structure of the merocyanins is intermediate between the Ia and Ib formulas, the absorption maximum is the arithmetical mean of the absorp-tion maxima of the corresponding symmetrical carbocyanin and monomethenylox-anine (II) (cf [6-10,3]). As a rule, however, the real structure of the mero-cyanin molecule approaches the covalent form (Ia), which should lead to a hyp-sochromic shift of the absorption maximum from the values calculated above, as is the case in the asymmetrical carbocyanins. The magnitude of this hypso-chromic effect will depend upon the closeness with which the structure of the dye approaches that of the formula (Ia), which in turn largely depends upon the basicity of the nitrogen-containing heterocyclic group [6].

Table 1 lists the absorption maxima of the two series of merocyanins we have synthesized: the derivatives of rhodanine and 3-ethylrhodanine, as well as of the corresponding carbocyanins and monomethenyloxanines. The dyes are listed in the order of diminishing hypsochromic effect, as given in the second column for each group of dyes.

TABLE 1

| Nitrogen-containing heterocyclic group | $\lambda$ max of the sym-carbocy-anin, (in m$\mu$) | Merocyanins | | | |
|---|---|---|---|---|---|
| | | Rhodanine derivatives | | 3-Ethylrhodanin derivatives | |
| | | max, (m$\mu$) | Hypsochromic effect, (m$\mu$) | max, (m$\mu$) | Hypsochromic effect, (m$\mu$) |
| 3,3-Dimethylindolenine | 546 | 500 | 43 | 503 | 40 |
| Benzoselenazole | 570 | 522 | 33 | 524 | 31 |
| $\alpha$-Naphthothiazole | 593 | 536 | 30.5 | 540 | 26.5 |
| $\beta$-Naphthothiazole | 595 | 540 | 27.5 | 542 | 25.5 |
| Benzothiazole | 557 | 520 | 28.5 | 524 | 24.5 |
| $\beta$-Naphthoxazole | 514 | 502 | 25 | 506 | 21 |
| Benzoxazole | 483 | 488 | 23.5 | 492 | 19.5 |
| 5-Methylthiodiazole-(1,3,4) | 513 | 511 | 15.5 | 514 | 12.5 |
| Thiazoline | 445 | 480 | 12.5 | 482 | 10.5 |
| Thiazole | 543 | 530 | 11.5 | 532 | 9.5 |
| Pyridine-(2) | 560 | 540 | 10 | 542 | 8 |
| Quinoline-(4) | 705 | 612 | 10.5 | 614 | 8.5 |
| Quinoline-(2) | 604 | 564 | 8 | 565 | 7 |
| 1-Methylbenzimidazole | 490 | 510 | 5 | 511 | 4 |

NOTE. The absorption maxima of the monomethenyloxanins (II) (R = H or $C_2H_5$) are located at 540 m$\mu$ in ethyl alcohol.

When we examine these results, the first thing we note is that the effect of the nature of a nitrogen-containing group upon the color of the merocyanins differs from that in the corresponding carbocyanins. N. N. Sveshnikov [10] has made similar observations in the merocyanins of 3-hydroxythionaphthene derivatives. As for the magnitude of the hypsochromic effect, it falls as the basicity of the nitrogen-containing heterocyclic group rises, as learned from a study of the absorption spectra of asymmetrical cyanins [11] and the ability of symmetrical carbocyanins to change into dibasic salts [12].

As we see from the table, the shift totals 40-43 m$\mu$ for merocyanins containing 3,3-dimethylindolenine radicals, and does not exceed 4-5 m$\mu$ for dyes with the most basic radical, benzimidazole. The merocyanins containing thiazoline, benzoxazole, and quinoline-(2) groups are somewhat out of line, their hypsochromic effect being smaller than one would expect from the degree of basicity of these groups. There is no fully satisfactory explanation for this fact at the present time. Thus, our findings confirm, on the whole, that the closer the structure of the tested merocyanins approaches to that of the covalent formula (Ia), the higher the color of these dyes. It should be noted that, in contrast to the corresponding dyes that contain 3-hydroxythionaphthene groups [13], the color of alcoholic solutions of salts of the monomethenyloxanines – derivatives of rhodanine and 3-ethylrhodanine – is practically unaffected by the addition of dilute mineral acids.

Most of the dimethylmerocyanins – rhodanine derivatives – are slightly

soluble in ethyl alcohol, which makes it hard to employ them as optical sen-
sitizers. Attaching an ethyl group to the nitrogen atom of the rhodanine resi-
due in these dyes increases their solubility in alcohol noticeably. The syn-
thesized merocyanins act as sensitizers of silver halide emulsions. The most
active are the dyes with thiazole, thiazoline and pyridine-(2) groups, the
quinoline-(4) derivatives being much poorer sensitizers than all the other com-
pounds, and also causing some fogging. The attaching of an ethyl group at the
3 position of the rhodanine residue always increases the dye's efficiency over
dyes that are derivatives of unsubstituted rhodanine.

## EXPERIMENTAL

### Synthesis of Intermediates

3-Ethyl-5-(acetanilinomethylene)-rhodanine. A solution of 4.8 g of 3-
ethylrhodanine and 6.45 g of diphenylformamidine in 35 ml of acetic anhydride
containing 0.85 ml of triethylamine was refluxed for 1.5 hours. The next day
the precipitated product was filtered out and washed with water and with alcohol.
After it had been dried (weight 5.3 g, m.p. 128-129°), the product was crystal-
lized from 60 ml of ethyl alcohol. The yield was 4.5 g (49% of the theoretical).
Light yellow needles with a m.p. of 133° (with decomp.) [14].

Found %: N 9.00. $C_{14}H_{14}O_2N_2S_2$. Calc. %: N 9.14.

2-(β-Acetanilinovinyl)-pyridine ethiodide. A mixture of 0.35 g of 2-(β-
anilinovinyl)-pyridine ethiodide [15], 0.074 g of ethyl orthoformate, and 2 ml
of acetic anhydride was refluxed for 1 hour at 120°. The reaction solution was
ice-chilled and treated with ether, the resultant precipitate being filtered out
and washed with ether. The yield was 0.31 g (78.5%); m.p. 135-136° (with decomp.).
The product was crystallized from butyl alcohol for analysis. This yielded 0.28
g of light-yellow platelets with a m.p. of 136-137° (with decomp.).

Found %: N 7.10. $C_{17}H_{19}ON_2I$. Calc. %: N 7.10.

Ethyl-p-toluenesulfonates of nitrogen-containing heterocyclic bases. These
were synthesized by heating equimolecular quantities of the base and ethyl p-
toluenesulfonate in a flask fitted with an air condenser and a calcium chloride
tube under the following conditions: 4 hours at 140° for 2-methylbenzothiazole,
2-methylbenzoselenazole, 2,3,3-trimethylindolenine, 2-methyl-α-naphthothiazole,
and 2-methyl-β-naphthothiazole; 5 hours at 140-145° for 2-methylthiazole; 1
hour at 120-130° for lepidine; and 1 hour at 110-115° for 1,2-dimethylbenzimi-
dazole. The quaternary salts were used without further refining in synthesizing
the dyes.

### Synthesis of Merocyanins

The conditions governing the synthesis of the merocyanins, the melting
points of the dyes, and the analysis results are given in Tables 2 and 3. The
following notation is employed in these tables – for the initial products:
I – rhodanine; II – 3-ethylrhodanine; III – 5-(acetanilinomethylene)-rhoda-
nine [16]; and IV – 3-ethyl-5-(acetanilinomethylene)-rhodanine; for the ethyl-
p-toluenesulfonates: V – of 2-methylbenzothiazole; VI – of 2-methyl-α-naphtho-
thiazole; VII – of 2-methyl-β-naphthothiazole; VIII – of lepidine; IX – of
2-methylbenzoselenazole; X – of 2,3,3-trimethylindolenine; XI – of 2-methyl-
thiazole; XII – 1,2-dimethylbenzimidazole; and XIII – 2-(β-acetanilinovinyl)-

-β-naphthoxazole; and for the ethiodides: XIV — 2-(β-acetanilinovinyl)-benzoxazole; XV — 2-(β-acetanilinovinyl)-5-methylthiodiazole-(1,3,4) [17]; XVI — 2-(β-acetanilinovinyl)-quinoline; XVII — 2-(β-acetanilinovinyl)-thiazole; and XVIII — 2-(β-acetanilinovinyl)-pyridine.

In every case the dye recovered upon chilling was filtered out, washed with water and with ethyl alcohol, and crystallized until its melting point was constant. The preparations were dried in vacuum at 50-60° to constant weight before being analyzed.

Triethylamine salt of 5-(4'-hydroxythiazolinethion-(2')-yl-5'-methylene)-thiazolidinethion-(2)-one-(4) [5]. A mixture of 0.55 g of 5-(acetanilinomethylene)-rhodanine, 0.53 g of rhodanine, 8 ml of pyridine, and 0.8 g of triethylamine was refluxed at 130° for 2 hours. After it had cooled, 200 ml of ether was added, and the precipitated dye was filtered out 6 hours later and washed with ether. Weight 0.38 g, m.p. 204-208° (with decomp.). 0.15 g (39.7% of the theoretical) was recovered after recrystallization from ethyl alcohol (1 g in 100 ml). Blue prisms with a m.p. of 226-228° (with decomp.). The salt was slightly soluble in benzene and ether, but readily soluble in ethyl alcohol and pyridine. The absorption maximum in ethyl alcohol was located at 540 m$\mu$.

Found %: N 9.69. $C_{17}H_{27}O_2N_3S_4$. Computed %: N 9.68.

Triethylamine salt of 3-ethyl-5-(3'-ethyl-4'-hydroxythiazolinethion-(2')-yl-5'-methylene)-thiazolinethion-(2)-one-(4). Like the preceding dye, this was synthesized by heating a mixture of 0.3 g of 3-ethyl-5-(acetanilinomethylene)-rhodanine, 0.32 g of 3-ethylrhodanine, 4 ml of pyridine, and 0.4 g of triethylamine to 130° for 2 hours. Weight 0.35 g, m.p. 170-172° (with decomp.). Recrystallization from benzene (1 g in 150 ml) yielded 0.25 g (80.8% of the theoretical). Red-violet prisms with a m.p. of 177-179° (with decomp.). The salt was slightly soluble in ether, but readily soluble in benzene, ethyl alcohol, and pyridine. Its absorption maximum in ethyl alcohol was located at 540 m$\mu$.

Found %: N 9.69. $C_{17}H_{27}O_2N_3S_4$. Calc. %: N 9.68.

The absorption maxima of all the synthesized dyes was measured with a Koenig-Martens spectrophotometer.

## SUMMARY

1. 28 Dimethylmerocyanins — derivatives of rhodanine and 3-ethylrhodanine — have been synthesized, differing in the nature of their nitrogen-containing heterocyclic residues, plus two monomethenyloxanine dyes — derivatives of rhodanine and 3-ethylrhodanine.

2. It has been shown that the absorption maxima of the dimethylmerocyanins — rhodanine derivatives — are shifted to shorter wavelengths, compared to the arithmetical mean values calculated from the absorption maxima of the corresponding symmetrical carbocyanin and monomethenyloxanine. It has been found that the magnitude of this hypsochromic effect depends upon the basicity of the nitrogen-containing heterocyclic residue.

3. All the synthesized merocyanins are sensitizers of silver halide emulsions, the most effective being the dyes containing thiazole, thiazoline, and pyridine-(2) groups.

TABLE 2

| Dye | g of III or IV | g of quaternary salt | Condensation conditions | | | |
|---|---|---|---|---|---|---|
| | | | Ml of $C_5H_5N$ | Ml of absolute $C_2H_5OH$ | Ml of $C_4H_9OH$ | Ml of $(C_2H_5)_3N$ |
| 5-(3'-Ethylbenzothiazolinylidene-2'-ethylidene)-thiazolidinethion-(2)-one-(4) [2] | III 0.5 | V 0.59 | 10 | - | - | - |
| 3-Ethyl-5-(3'-ethylbenzothiazolinylidene-2'-ethylidene)-thiazolidine-thion-(2)-one-(4) [2] | IV 0.3 | V 0.3 | 3 | - | - | - |
| 5-(3'-Ethyl-6',7'-benzobenzothiazolinylidene-2'-ethylidene)-thiazolidinethion-(2)-one-(4) [2] | III 0.28 | VI 0.4 | 6 | - | - | - |
| 3-Ethyl-5-(3'-ethyl-6',7'-benzobenzothiazolinylidine-2'-ethylidene)-thiazolidinethion-(2)-one-(4) [2] | IV 0.3 | VI 0.4 | 3 | - | - | - |
| 5-(3'-Ethyl-4',5'-benzobenzothiazolinylidene-2'-ethylidene)-thiazolidinethion-(2)-one-(4) [4] | III 0.28 | VII 0.4 | - | 10 | - | 0.14 |
| 3-Ethyl-5-(3'-ethyl-4',5'-benzobenzothiazolinylidene-2'-ethylidene)-thiazolidinethion-(2)-one-(4) [4] | IV 0.3 | VII 0.4 | 3 | - | - | - |
| 5-(1'-Ethyldihydroquinolylidene-4'-ethylidene)-thiazolidinethion-(2)-one-(4) [2,4] | III 0.87 | VIII 1.03 | 1.25 | - | 2.5 | 0.4 |
| 3-Ethyl-5-(1'-ethyldihydroquinolylidene-4'-ethylidene)-thiazolidinethion-(2)-one-(4) [2] | IV 0.73 | VIII 0.6 | 1.25 | - | 2.5 | 0.28 |
| 5-(1'-Ethyl-3',3'-dimethylindolinylidene-2'-ethylidene)-thiazolidinethion-(2)-one-(4) | III 0.28 | X 0.26 | - | - | 5 | 0.14 |
| 3-Ethyl-5-(1'-ethyl-3',3'-dimethylindolinylidene-2'-ethylidene)-thiazolidinethion-(2)-one-(4) | IV 0.3 | X 0.31 | 3 | - | - | - |
| 5-(3'-Ethylthiazolinylidene-2'-ethylidene)-thiazolidinethion-(2)-one-(4) | III 0.42 | XI 0.45 | - | - | 6 | 0.21 |
| 3-Ethyl-5-(3'-ethylthiazolinylidene-2'-ethylidene)-thiazolidinethion-(2)-one-(4) | IV 0.6 | XI 0.6 | - | - | 3 | 0.28 |
| 5-(1'-Methyl-3'-ethylbenzimidazolinylidene-2'-ethylidene)-thiazolidinethion-(2)-one-(4) | III 0.55 | XII 0.72 | 1 | - | 2 | 0.28 |
| 3-Ethyl-5-(1'-methyl-3'-ethylbenzimidazolinylidene-2'-ethylidene)-thiazolidinethion-(2)-one-(4) | IV 0.3 | XII 0.36 | - | - | 3 | 0.14 |
| 5-(3'-Ethylbenzoselenazolinylidene-2'-ethylidene)-thiazolidinethion-(2)-one-(4) | III 0.28 | IX 0.42 | 6 | - | - | - |
| 3-Ethyl-5-(3'-ethylbenzoselenazolinylidene-2'-ethylidene)-thiazolidinethion-(2)-one-(4) | IV 0.3 | IX 0.42 | 6 | - | - | - |

TABLE 2

| Boiling time, min. | Yield, % of theory | Crystallization, solvent and quantity used, ml per g of dye | Appearance | Melting point | % N found | Calculated Empirical formula | % N |
|---|---|---|---|---|---|---|---|
| 20 | 65.6 | Pyridine 50 | Red-violet needles | 276° | — | $C_{14}H_{12}ON_2S_3$* | — |
| 15 | 63.2 | Glacial acetic acid 300 | Dark-red needles | 262-264 | 8.17 | $C_{16}H_{16}ON_2S_3$ | 8.03 |
| 60 | 32.4 | Alcohol + pyridine (4:1) 1100 | Minute dark-brown needles | 286-288 | 7.57 | $C_{18}H_{14}ON_2S_3$ | 7.50 |
| 120 | 40.2 | Glacial acetic acid 250 | Minute violet needles | 260-262 | 6.91 | $C_{20}H_{18}ON_2S_3$ | 7.02 |
| 20 | 32.4 | Glacial acetic acid 2000 | Minute dark-green needles | 288-290 | 7.57 | $C_{18}H_{14}ON_2S_3$ | 7.75 |
| 180 | 55.3 | Glacial acetic acid 330 | Dark-red needles with a green sheen | 274-276 | 7.21 | $C_{20}H_{18}ON_2S_3$ | 7.02 |
| 60 | 28.6 | Glacial acetic acid 40 | Lustrous dark-blue leaflets | 252-254 | 8.89 | $C_{16}H_{14}ON_2S_2$ | 8.91 |
| 60 | 76.1 | Benzene 120 | Dark-blue needles | 226-227 | 8.15 | $C_{18}H_{18}ON_2S_2$ | 8.18 |
| 30 | 45.4 | Ethyl alcohol 200 | Bright-red needles | 218 | 8.36 | $C_{17}H_{18}ON_2S_2$ | 8.47 |
| 30 | 61.4 | Ethyl alcohol 250 | Pink leaflets | 193-195 | 7.71 | $C_{18}H_{20}ON_2S_2$ | 7.81 |
| 40 | 46.8 | Ethyl alcohol 800 | Brown prisms | 239-241 | 10.35 | $C_{10}H_{10}ON_2S_3$ | 10.35 |
| 40 | 58.7 | Ethyl alcohol 100 | Dark-blue prisms | 216-217 | 9.30 | $C_{12}H_{14}ON_2S_3$ | 9.38 |
| 60 | 18.9 | Ethyl alcohol 680 | Minute red-brown needles | 217-218 | 13.00 | $C_{15}H_{15}ON_3S_2$ | 13.23 |
| 120 | 52 | Ethyl alcohol 400 | Red needles | 251-252 | 12.07 | $C_{17}H_{19}ON_3S_2$ | 12.16 |
| 60 | 44.9 | Glacial acetic acid 650 | Violet prisms | 240-241 | 7.69 | $C_{14}H_{12}ON_2S_2Se$ | 7.62 |
| 30 | 46 | Glacial acetic acid 400 | Minute red-brown needles | 258-260 | 7.00 | $C_{18}H_{18}ON_2S_2Se$ | 7.08 |

*The per cent S was determined for this dye: Found 29.77, Calc. 30.0.

TABLE 3

| Dye | g of acetanilino-vinyl product | g of I or II | Condensation conditions | | | |
|---|---|---|---|---|---|---|
| | | | Ml of $C_5H_5N$ | Ml of absolute $C_2H_5OH$ | Ml of $C_4H_9OH$ | Ml of $(C_2H_5)_3N$ |
| 5-(3'-Ethylbenzoxazolinylidene-2'-ethylidene)-thiazolidinethion-(2)-one-(4) [2] | XIV 1.74 | I 0.67 | – | 10 | – | 0.74 |
| 3-Ethyl-5-(3'-ethylbenzoxazolinylidene-2'-ethylidene)-thiazolidinethion-(2)-one-(4) | XIV 0.87 | II 0.32 | – | 10 | – | 0.28 |
| 5-(3'-Ethyl-4',5'-benzobenzoxazolinylidene-2'-ethylidene)-thiazolidinethion-(2)-one-(4) | XIII 0.25 | I 0.06 | 5 | – | – | – |
| 3-Ethyl-5-(3'-ethyl-4',5'-benzobenzoxazolinylidene-2'-ethylidene)-thiazolidinethion-(2)-one-(4) | XIII 0.53 | II 0.16 | 5 | – | – | – |
| 5-(3'-Ethyl-5'-methylthiodiazolinylidene-2'-ethylidene)-thiazolidinethion-(2)-one-(4) | XV 0.4 | I 0.13 | 5 | – | – | – |
| 3-Ethyl-5-(3'-ethyl-5'-methylthiodiazolinylidene-2'-ethylidene)-thiazolidinethion-(2)-one-(4) | XV 0.8 | II 0.32 | 10 | – | – | – |
| 5-(1'Ethyldihydropyridylidene-2'-ethylidene)-thiazolidinethion-(2)-one-(4) | XVIII 0.39 | I 0.13 | – | – | 5 | 0.14 |
| 3-Ethyl-5-(1'-ethyldihydropyridylidene-2'-ethylidene)-thiazolidine-(2)-one-(4) | XVIII 0.39 | II 0.16 | – | 5 | – | 0.14 |
| 5-(1'-Ethyldihydroquinolylidene-2'-ethylidene)-thiazolidinethion-(2)-one-(4) [4] | XVI 1.32 | I 0.47 | 10 | – | – | – |
| 3-Ethyl-5-(1'-ethyldihydroquinolylidene-2'-ethylidene)-thiazolidinethion-(2)-one-(4) [2] | XVI 0.44 | II 0.19 | 5 | – | – | – |
| 3-Ethyl-5-(3'-ethylthiazolidinylidene-2'-ethylidene)-thiazolidinethion-(2)-one-(4) | XVII 0.4 | II 0.16 | 1.5 | – | 3 | 0.14 |
| 5-(3'-Ethylthiazolidinylidene-2'-ethylidene)-thiazolidinethion-(2)-one-(4) [9] | XVII 0.4 | I 0.13 | 1 | – | 2 | 0.14 |

TABLE 3

| Boiling time, min. | Yield % of theory | Crystallization, solvent and quantity used, ml per g of dye | Appearance | Analysis | | | |
|---|---|---|---|---|---|---|---|
| | | | | Melting point | % N found | Calculated | |
| | | | | | | Empirical formula | % N |
| 20 | 58.8 | Glacial acetic acid 330 | Bright-red leaflets | 282° | 9.11 | $C_{14}H_{12}O_2N_2S_2$ | 9.20 |
| 15 | 52.7 | Benzene 150 | Dark-pink leaflets | 228-230 | 8.48 | $C_{16}H_{16}O_2N_2S_2$ | 8.42 |
| 120 | 56.6 | Ethyl alcohol — pyridine (4:1) mixture 715 | Red-violet needles | 268-270 | 7.92 | $C_{18}H_{14}O_2N_2S_2$ | 7.90 |
| 60 | 70 | Glacial acetic acid 250 | Minute red needles | 302-304 | 7.50 | $C_{20}H_{17}O_2N_3S_2$ | 7.32 |
| 30 | 31.6 | Glacial acetic acid 220 | Bright-pink needles | 274-276 | 14.89 | $C_{10}H_{11}ON_3S_3$ | 14.73 |
| 30 | 47.8 | Ethyl alcohol 800 | Red needles | 244-246 | 13.48 | $C_{12}H_{15}ON_3S_3$ | 13.40 |
| 30 | 56.6 | Ethyl alcohol 600 | Lustrous dark-blue prisms | 218-220 | 10.39 | $C_{12}H_{12}ON_2S_2$ | 10.59 |
| 30 | 75.3 | Ethyl alcohol 50 | Violet leaflets | 162-164 | – | $C_{14}H_{16}ON_2S_2$* | – |
| 360 | 46.7 | Ethyl alcohol 12,500 | Lustrous dark-blue leaflets | 256-258 | 8.68 | $C_{16}H_{14}ON_2S_2$ | 8.91 |
| 360 | 38 | Benzene 100 | Lustrous blue prisms | 233-235 | 8.06 | $C_{18}H_{18}ON_2S_2$ | 8.18 |
| 120 | 70 | Ethyl alcohol 75 | Brown leaflets with a blue sheen | 163-164 | 9.38 | $C_{12}H_{16}ON_2S_3$ | 9.32 |
| 60 | 71 | Ethyl alcohol 400 | Brown prisms | 260-262 | 10.42 | $C_{10}H_{12}ON_2S_3$ | 10.28 |

* The per cent S was determined for this dye: Found 21.77, Calc. 21.92.

# LITERATURE CITED

[1]  J. D. Kendall, J. Soc. Dyers and Colourists, 52, 13 (1936): Congr. Photogr. Sci. appl. Proces-verbeaux, 9, 227 (1936).

[2]  Kodak-Pathe. French Patent 793722; Ilford Ltd. British Patent 450958; Kodak Ltd.  British Patent 466244.

[3]  L. G. S. Brooker, Frontiers in Chemistry, III, 63 (1945).

[4]  Ilford Ltd. British Patent 428222; Kodak-Pathe. French Patent 48226 (supplement to French Patent 793722).

[5]  Eastman Kodak Co. U.S. Patent 2241238.

[6]  A. I. Kiprianov and G. T. Pilyugin, Sci. Rep. Kharkov State Univ. 10, 104 (1937).

[7]  A. I. Kiprianov and V. E. Petrunkin, J. Gen. Chem. 10, 613 (1940); Proc. USSR Acad. Sci. 1939, No. 4, 27.

[8]  A. I. Kiprianov, Jubilee Symposium USSR Acad. Sci. I, 254 (1944); Sci. Rep. Kiev. State Univ. 5, 135 (1946).

[9]  A. I. Kiprianov and E. S. Timoshenko, J. Gen. Chem. 17, 1468 (1947).

[10]  N. N. Sveshnikov, I. I. Levkoev, and V. V. Durmashkina, J. Gen. Chem. 14, 198 (1944).

[11]  L. G. S. Brooker, Rev. of modern Phys., 14, 275 (1942).

[12]  A. I. Kiprianov, S. G. Fridman, and L. S. Pupko, Trans. Inst. Org. Chem. Acad. Sci. USSR 13, 40 (1947).

[13]  N. N. Sveshnikov and I. I. Levkoev, J. Gen. Chem. 10, 274 (1940).

[14]  Kodak-Pathe. French Patent 49385 (supplement to French Patent 793722).

[15]  T. Ogata, J. Chem. Soc. Japan, 55, 394 (1934): Kodak Ltd. British Patent 609814.

[16]  Z. P. Sytnik, I. I. Levkoyev, and M. V. Deichmeister, J. Gen. Chem. 21, 768*(1951).

[17]  Gevaert, Photo Prod. N. O., French Patent 796789.

*See C.B. English translation, p. 847.

# SOME COMMENTS ON DETERMINING THE PURITY OF 2,5-DIMETHYLPYRROLE AND PYRROLE

N. M. Timoshevskaya

The Syntheses of Organic Preparations, Vol. 2, published in 1949, states: "Since 2,5-dimethylpyrrole forms no solid derivatives, the refractive index, $n_D^{22}$ 1.500, may be employed as a criterion of the purity of the freshly distilled product."

This assertion is not entirely right. We have found that the freezing point may also be used as a criterion of the purity of 2,5-dimethylpyrrole. Investigation has shown that 2,5-dimethylpyrrole solidifies at +6.5° C. The apparatus for the freezing point determination consists of a test tube containing a glass stirrer and a thermometer (preferably graduated in tenths of a degree). Enough 2,5-dimethylpyrrole is poured into the test tube to immerse the mercury bulb of the thermometer in the liquid. The test tube thus equipped is placed within another test tube immersed in a beaker containing ice water. The thermometer readings are taken every 30 seconds. The temperature usually drops to +3.5-4.5°C, and then rises quickly to +6.5°, the contents of the test tube beginning to solidify at that instant. After some time has elapsed the temperature begins to drop, and the substance is so solid that stirring becomes impossible.

The 2,5-dimethylpyrrole was prepared by heating 2,5-dimethylpyrrole-monocarboxylate with soda lime [1].

Preliminary tests were also run to determine the freezing point of pyrrole, the tests being made in the apparatus described above, with the test tube immersed in a Dewar flask filled with dry ice. The freezing point of pyrrole is of the order of −27° C.

## LITERATURE CITED

[1] Timoshevskaya, J. Gen. Chem. 9, 766 (1939).

**BLANK PAGE**